VOL. XVIII. OCTOBER, 1896. NO. 8.

AMERICAN

CHEMICAL JOURNAL.

ON TRIMETAPHOSPHIMIC ACID AND ITS DECOMPOSITION-PRODUCTS.[1]

BY H. N. STOKES.

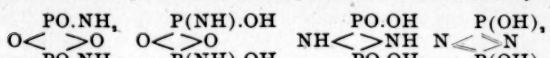
In a paper on the chloronitrides of phosphorus,[2] I mentioned, by way of preliminary notice, that Liebig's chloronitride, $P_3N_3Cl_6$, by appropriate treatment gives an acid, $P_3N_3O_4H_6$, to which I gave the name *trimetaphosphimic acid*. The object of the present paper is to describe in detail the properties and decomposition-products of this, the third member of the metaphosphimic acid series.

In the preliminary notice a metaphosphimic acid was defined as a metaphosphoric acid, $(PO_3H)_n$, in which one-third of the oxygen is replaced by an equivalent number of imide groups, NH, *i. e.*, $(PNO_2H_3)_n$. It was further pointed out that for each acid of this formula, with the exception of the simplest, at least four forms are theoretically possible, two of which are direct substitution-products of the corresponding metaphosphoric acid, containing a nucleus consisting of phosphorus atoms united by oxygen, the other two belonging to a different type, in which the phosphorus atoms are united by nitrogen. This was illustrated by the acid, $P_3N_3O_4H_6$, none of the

[1] The work described in this paper and the following one on tetrametaphosphimic acid was done in the chemical laboratory of the United States Geological Survey, and I wish to acknowledge my indebtedness to the Director, Hon. C. D. Walcott, and to Prof. F. W. Clarke, for the facilities placed at my disposal.

[2] THIS JOURNAL, 17, 275, (1895) : also Ber. d. chem. Ges., 28, 437.

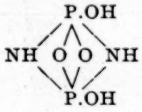
forms of which, it is true, are as yet known with certainty:



(*a*) (*b*) (*c*) (*d*)

Dimetaphosphoryl amide. ——— Dimetaphosphimic acid. Diphosphonitrilic acid.

A fifth form might be added:



containing at the same time both the metaphosphoric and the metaphosphimic nucleus.

Schiff[1] described a body to which he gave the name *Phosphaminsaeure*, formed by acting on phosphorus pentoxide with dry ammonia, and which, according to his analyses, has the formula PNO_2H_2.[2] According to Gladstone and Holmes,[3] Schiff's acid is probably a mixture of pyrophosphodiamic and metaphosphoric acids. As Schiff failed to publish nitrogen determinations for his salts, it still remains a question whether a metaphosphimic acid can be produced in this way.

Gladstone, who was the first to devote much attention to phosphorus chloronitride, obtained from it by the action of aqueous ether and of alcoholic alkalies,[4] an acid which he first called deutazophosphoric acid and later pyrophosphodiamic acid, and to which he gave the formula $P_2N_2O_4H_6$, regarding it as the diamide of pyrophosphoric acid[5]

$$O<\begin{matrix}PO(OH)NH_2\\PO(OH)NH_2\end{matrix}.$$

While I am not prepared to deny positively the correctness

[1] Ann. Chem. (Liebig), **103**, 168, (1857).

[2] I have elsewhere pointed out (This JOURNAL, **18**, 198,) that Schiff's acid has been erroneously described in some of the reference books as amidophosphoric acid, a body which I was the first to obtain.

[3] J. Chem. Soc., [2], **2**, 229, 233, 235.

[4] Q. J. Chem. Soc., **3**, 135, 354; Ann. Chem. (Liebig), **76**, 79; **77**, 315; J. Chem. Soc. [2], **2**, 231.

[5] J. Chem. Soc., [2], **6**, 69.

of the formula deduced by Gladstone, and to assert that no such acid can be obtained in this way from phosphorus chloronitride, yet the facts as stated by him are capable of another interpretation, namely, that his acid is not the diamide of pyrophosphoric acid, but trimetaphosphimic acid.

It will be seen that

$$P_2N_2O_4H_4M'_2 = P_2N_2O_4H_2M'_2 + H_2O,$$

Pyrophosphodiamate.

the latter being identical in empirical composition with $P_3N_3O_6H_4M'_2 + 1\frac{1}{2}H_2O$, *i. e.*, a trimetaphosphimate with $1\frac{1}{2}H_2O$. Hence the latter, if containing this amount of water, might be mistaken for a pyrophosphodiamate. The only salts made by Gladstone directly from the chloride, $P_3N_3Cl_6$, were the silver and barium salts; the others were made from a supposed pyrophosphodiamate obtained from phosphorus oxychloride and ammonia, and there is no proof in Gladstone's papers of the identity of the acids from both sources. His figures for the barium salt were, as he admits, not satisfactory, while the analyses of the silver salt were made with a crude preparation, for the purity of which there is no guarantee. I have myself found that barium trimetaphosphimate varies considerably in composition, contains water, and is hygroscopic. Sodium trimetaphosphimate is the only well-defined substance I have been able to obtain by decomposing the chloronitride by alcoholic soda, and the salt is so characteristic as hardly to be mistaken. It seems quite possible, therefore, that Gladstone actually had crude trimetaphosphimic acid in hand and failed to recognize its true nature only because of the unfortunate selection of salts which are amorphous, hydrated, and difficult to obtain pure.

In a paper of much later date Mente[1] described several acids obtained by the successive action of ammonium carbamate and water on phosphorus oxychloride. Among them is one to which he gave the name diimidodiphosphoric acid and the formula, $NH<\begin{matrix}PO.OH\\PO.OH\end{matrix}>NH$, and which he regards as identical with Gladstone's pyrophosphodiamic acid. If Mente's formula

[1] Ann. Chem. (Liebig), **247**, 239, 244, (1888).

is correct, it is the second, or *dimetaphosphimic* acid. I have been unable to repeat Mente's work, and his data are too meagre to admit of a positive conclusion, either as to its molecular weight or even its empirical composition, but it appears not to be identical with trimetaphosphimic acid.

Constitution of Trimetaphosphimic Acid.

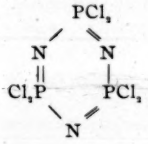
Although trimetaphosphimic acid is an uncrystallizable and unstable body, it forms stable salts, several of which crystallize in characteristic forms. Three atoms of hydrogen are replacable by alkali metals, while silver is able to replace either three or six. The following are the most noteworthy:

$P_3N_3O_6H_3Na_3 + 4H_2O$—Rhombic prisms.
$P_3N_3O_6H_3Na_3 + H_2O$—Slender prisms.
$P_3N_3O_6H_3(NH_4)_3 + H_2O$—Scales.
$P_3N_3O_6H_3NaBa + 1\frac{1}{2}H_2O$—Rhombohedra.
$P_3N_3O_6H_3Ag_3$—Monoclinic prisms.
$PN_2O_2Ag_2$—Two forms, white and red.

The first, third and fifth serve to identify the acid. The tertiary silver salt, being anhydrous and easily obtained pure, establishes its empirical formula. Those salts which contain water of crystallization do not lose it completely at any temperature short of decomposition, leaving open the question whether the acid may not have the formula $P_3N_3O_3H_3$.

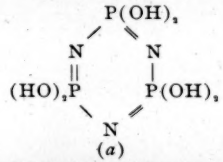
The constitution of trimetaphosphimic acid depends on that of the chloronitride $P_3N_3Cl_6$. The structural formula of the latter has not yet been definitely established, but the following data are available. It is reasonably certain that in the chloronitride phosphorus atoms are united by nitrogen atoms. Its formation from phosphorus pentachloride and ammonia is best explained on this assumption, as is its decomposition into orthophosphoric acid and ammonia. If phosphorus were united to phosphorus and nitrogen to nitrogen, the formation of reducing phosphoric acids or of hydrazine might be expected. Neither is it likely that chlorine is united to nitrogen, for in this case hydroxylamine might be expected to result. Several structural formulas are possible, which meet this requirement, the simplest being that in which the nucleus

consists of a symmetrical ring of three phosphorus and three nitrogen atoms.



or a similar one with diagonal or "centric" union.

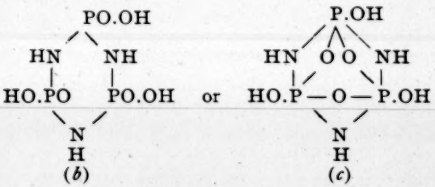
Direct replacement of chlorine by hydroxyl would then give



(*a*)

Triphosphonitrilic acid.

The labile nature of the hydrogen atoms in nitrogenous bodies, as observed in many organic compounds, makes it by no means improbable that an acid of this form may of itself, or under the influence of reagents, undergo transformation into the tautomeric form:

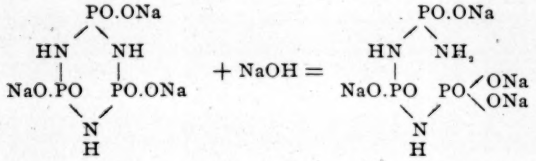


(*b*) (*c*)

Trimetaphosphimic acid.

An acid of the form (*a*) may be expected to give two sodium salts in which respectively three and six atoms of hydrogen are replaced. A salt with six atoms of sodium cannot be produced, however, by any method which I have tried. The only salt besides the ordinary one with three atoms of

sodium s one with *four* atoms, and this is formed in the presence of a large excess of caustic soda ; it is very unstable and is reconverted into the three-atom salt by repeated precipitation from aqueous solution by alcohol. It is not obvious why an acid of the form (*a*) should give such a salt. If we assume that (*b*) represents the correct formula, and that the acid is the symmetrical inner anhydride or lactam of an open chain acid, we may regard this salt as being formed by addition, thus :



the latter being a salt of *amido-diimidotriphosphoric acid.*[1] Unfortunately I have been unable to prove this with certainty. A silver salt of the composition $P_3N_3O_4H_4Ag_4$ would render it extremely probable, as all silver salts of phosphorus nitrogen acids hitherto observed are free from crystal water. A salt with four atoms of silver can be obtained from the above four-atom sodium salt, but it is very unstable and its composition does not agree with sufficient sharpness with that of the cyclic or open chain form to establish either formula definitely.

I am therefore inclined to give preference to formula (*b*). It seems likely, however, that salts of triphosphonitrilic acid may also exist. The hexa-silver salt has been observed in two well defined forms, as well as a third, possibly intermediate one. One of these is white, amorphous and soluble in ammonium nitrate ; it is easily converted into the other of identical composition, which is red, crystalline and insoluble in the same reagent. The colorless salt probably contains silver united to oxygen only, while in the other one-half is united to nitrogen.

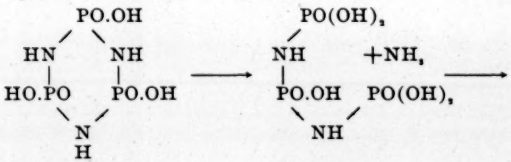
[1] The acids $PO(OH)_2.O.PO(OH)_2$ and $PO(OH)_2.O.PO(OH).O.PO(OH)_2$ being frequently designated as di- and triphosphoric acid, I call those in which the linking oxygen is replaced by imide, NH, *imido*-di- and triphosphoric acid.

Decomposition-Products of Trimetaphosphimic Acid.

An aqueous solution of trimetaphosphimic acid or of one of its salts acidified with one of the stronger mineral acids, decomposes slowly in the cold, rapidly on heating, the ultimate products being orthophosphoric acid and ammonia. If, however, the action be limited, there results a mixture of intermediate acids. The analysis of this mixture, which involved many experimental difficulties, proved the presence of the following:

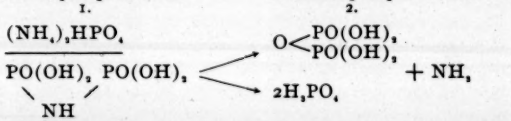
1. Unchanged trimetaphosphimic acid, $P_3N_3O_6H_6$.
2. Diimidotriphosphoric acid, $P_3N_3O_5H_5$.
3. Imidodiphosphoric acid,[1] $P_2NO_4H_5$.
4. Pyrophosphoric acid, $P_2O_7H_4$.
5. Orthophosphoric acid, PO_4H_3.

Assuming formula (*b*) for trimetaphosphimic acid, its decomposition would be thus represented:



Trimetaphosphimic acid. 1.

Diimidotriphosphoric acid. 2.



Imidodiphosphoric acid. 3.

4 and 5.

The second acid is important as a connecting link, proving that trimetaphosphimic acid actually has the triple formula $(PNO_2H_2)_3$. Most remarkable is the formation of pyrophosphoric acid, which occurs directly from imidodiphosphoric acid. The facts are these: If sodium imidodiphosphate be weakly acidified with acetic acid and boiled from five to ten

[1] This acid has the same composition and is probably identical with Gladstone's azophosphoric or pyrophosphamic acid. J. Chem. Soc., [2], **6**, 66, etc.

minutes, not more than fifteen per cent. is converted into pyrophosphoric acid and the remainder into orthophosphoric acid. Control experiments with sodium pyrophosphate showed that under the same conditions but a small portion is converted into orthophosphoric acid, ninety per cent. of the pyrophosphate being recovered. The pyrophosphoric acid is therefore not an intermediate product, but the imidodiphosphate is converted for the greater part directly into orthophosphoric acid, and in a much less degree into pyrophosphoric acid.

The above formula of imidodiphosphoric acid containing the group P—NH—P, follows directly from that of trimetaphosphimic acid. In view of the ease with which the condensed phosphoric acids split up in aqueous solution into orthophosphoric acid, while the reverse never occurs, it is difficult to see how the action of water or acids on a body of the assumed formula could give pyrophosphoric acid. If we adopt Gladstone's formula[1] $O\begin{cases}PO<^{NH_2}_{OH}\\ PO(OH)_2\end{cases}$, we can explain the formation of pyrophosphoric acid, but must at the same time assume that somewhere in the series the group P—N—P has been converted into P—O—P, for in the chloronitride, $P_2N_2Cl_4$, phosphorus can be united only by nitrogen. If the acid were really the amide of pyrophosphoric acid, boiling with acetic acid would first convert it into pyrophosphoric acid which, as above shown, is fairly stable under the observed conditions, and should be found present to the extent of at least ninety per cent. instead of only fifteen per cent. On this ground, it seems to me, we must reject the amidopyrophosphoric formula, and regard the body as imidodiphosphoric acid,

$$NH<^{PO(OH)_2}_{PO(OH)_2}.$$

This formula does not account for the pyrophosphoric acid. We may, perhaps, conceive that owing to the greater affinity of phosphorus for oxygen than for nitrogen, a group,

[1] J. Chem. Soc., [2], 6, 70.

$PO.(OH)_2$, is able to change places with a hydroxylic hydrogen atom.

$$\begin{array}{l} HO.PO.O{-}H \\ \quad | \\ HN{-}PO(OH)_2 \end{array} = \begin{array}{l} HO.PO.O{-}PO(OH)_2 \\ \quad | \\ HN{-}H \end{array}$$

the latter, in common with other amido phosphoric acids, being unstable, and passing easily into pyrophosphoric acid. It may be noted that this transformation seems to be promoted by heat, apparently more pyrophosphoric acid being formed by decomposing trimetaphosphimic acid in hot than in cold solution.

The second acid of the series, diimidotriphosphoric acid, seems really to have the constitution,

$$PO(OH)_2.NH.PO(OH).NH.PO(OH)_2,$$

implied by the name. It forms an acid salt with three, and a neutral salt with five atoms of silver, both of which are colorless. If it were a diamide of triphosphoric acid,

$$\begin{matrix} NH_2 \\ HO \end{matrix}\!\!>\!PO.O.PO(OH).O.PO\!<\!\!\begin{matrix} NH_2 \\ OH \end{matrix},$$

the penta-silver salt would have two atoms united to nitrogen, and such a salt, to judge from all phosphorus-nitrogen salts, where this is known to be the case, would be distinctly colored.

Still another intermediate acid is possible, preceding imidodiphosphoric acid, *viz.*, *amidoimidodiphosphoric acid*,

$$\begin{matrix} NH_2 \\ HO \end{matrix}\!\!>\!PO.NH.PO(OH)_2.$$

I have been unable to detect this acid thus far, but the too high percentage of nitrogen invariably found in imperfectly purified imidodiphosphoric acid, may be due to the presence of small amounts of this body.

In giving formulas to these bodies, I wish to be understood as using them with full appreciation of their uncertainty. A much more exhaustive study is necessary before they can be regarded as established as firmly as those of many organic compounds. There are several directions in which such a study might be of value. Besides the question of tautomerism, the stereochemistry of nitrogen might be attacked

with profit from this side. The analogy of nitrogen and phosphorus suggests the possibility of steric phenomena being shown by the latter also. The formula (*b*) suggested for trimetaphosphimic acid, for example, may imply a cis- and cis-trans-form depending on the position of the hydroxyls as well as of the imide hydrogen atoms, in short, quite a number of stereo-isomers may be conceived. I have thus far sought in vain for indications of the existence of such forms.

Finally, I would add that I have no desire to reserve for myself the study of these bodies, either from the above or from any other point of view.

Experimental Part.

Analytical Methods.—Salts of trimetaphosphimic acid and derived bodies are easily decomposed by fusion with sodium carbonate. As the process involves oxidation it is essential to keep the mass in a state of fusion for some time with access of air. Salts of silver of other easily reducible metals and those in which it is desired to determine alkali or nitrogen, must be decomposed by strong sulphuric acid. The substance, contained in a platinum crucible, is first moistened with dilute, and then covered with 4 or 5 cc. strong sulphuric acid, and the covered crucible heated to fuming for an hour in a radiator, care being taken that the fumes do not escape. In determining alkali metal, the resulting phosphoric acid may be conveniently removed by the ferric chloride—acetate method. As the water of crystallization cannot be completely expelled by heat without partial decomposition, it is best determined, together with the hydrogen of the salt proper, by combustion. This is conveniently carried out in a short combustion tube with a 10 cm. spiral of oxidized copper gauze, the substance, contained in a boat, being covered with fused potassium bichromate. As nitrous fumes are formed in abundance, the usual precautions must be taken. In the following, where more than one determination is given, the numbers always refer to different preparations.

Preparation of Trimetaphosphimic Acid.—The sodium salt affords the starting material for all preparations of trimetaphosphimic acid. It may be obtained by saponifying triphos-

phonitrilic chloride by alcoholic soda, but with much loss, owing to the formation of ethers and other substances of unknown nature. The chloride, as observed by Liebig and by Gladstone, is practically unacted on either by water or anhydrous ether, but as I have pointed out elsewhere[1] its decomposition may readily be effected by shaking its ethereal solution protractedly with water, whereby intimate contact is secured. Decomposition by ether and water alone, however, results in much loss, as the liberated hydrochloric acid rapidly decomposes trimetaphosphimic acid. The following method is perfectly satisfactory and gives practically the theoretical yield.

30 grams of the chloride are dissolved in 150 cc. ether free of alcohol, and the solution gently agitated with a solution of 110 grams crystallized sodium acetate in 200 cc. water, the agitation being conveniently effected by slowly rotating with a small turbine. After about fifteen hours, well formed crystals of the sodium salt begin to appear, and about seventy or eighty hours are required for complete decomposition. This point is best observed by evaporating a few drops of the ether and taking up the residue with water, any undecomposed chloride remaining undissolved. It is best to continue the agitation for a short time longer in order to decompose the chlorhydrines,[2] which are always formed as intermediate products. At the end of the operation nearly all the sodium salt has crystallized out, being almost insoluble in the strong salt solution; a further small amount can be recovered by mixing the solution with alcohol. After washing with 50 per cent. alcohol, the salt is pure enough for most purposes, but may be redissolved in water and precipitated by gradual addition of alcohol.

The same salt also results by decomposing triphosphonitrilic tetrachlorhydrine[3] with soda. It exists in two forms, apparently differing only in the amount of crystal water, the α-salt being formed at ordinary temperatures, the β-salt only above 80°.

α-Sodium Trimetaphosphimate, $P_3N_3O_6H_2Na_3 + 4H_2O$.—

[1] This JOURNAL, 17, 284. [2] *Ibid.*, 17, 285. [3] *Ibid.*, 17, 285.

The air-dried salt, prepared as above, gave the following figures:

	Calculated for $P_3N_3O_4H_3Na_3 + 4H_2O$.	Found. (1)	(2)
P	24.79	24.74	24.82
N	11.22	11.26	
Na	18.41	18.45	18.43
H	2.94	3.05	2.97

(1) P : N : Na : H = 3 : 3.02 : 3.01 : 11.47.

(2) P : Na : H = 3 : 2.97 : 11.

It loses weight slowly *in vacuo*, and 3 molecules of water are given off on long heating at 100°. After 5 hours at 100° the loss was:

	Calculated for $3H_2O$.	Found.
Loss	14.38	14.05

This is one of the most characteristic salts of trimetaphosphimic acid. It forms brittle orthorhombic prisms, usually about 1–2 mm. across, of which Fig. 1 represents the most common form.

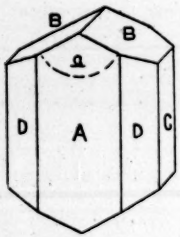


Fig. 1.

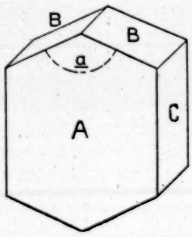


Fig. 2.

$A = \infty P \overline{\infty}$. $C = \infty P \breve{\infty}$.

$B = P \breve{\infty}$. $D = \infty P$.

The angle *a*, measured roughly under the microscope, is about 130°. No other faces are ever observed, and D is frequently lacking, giving the form shown in Fig. 2, which is often seen to be elongated in the direction of any one of the axes. They are especially well developed when slowly thrown down by acetic acid and alcohol from alkaline solution; when formed by rapid addition of alcohol in large excess they

tend to elongation in the direction of the principal axis, being often acicular, often long flat prisms with imperfectly developed ends.

At 20°, 100 parts water dissolve 18.3 parts; in hot water it is much more soluble, and from its hot solution it crystallizes but slowly; the larger crystals dissolve in hot water with a decrepitating sound. The reaction towards litmus is neutral. On rapidly heating the dry salt it gives off water and later ammonia, and fuses to a clear glass. It is but slowly decomposed by boiling with water; after three hours heating traces of phosphoric and imidodiphosphoric acid were shown by magnesia mixture. Alkalies do not cause the evolution of any appreciable quantity of ammonia, even when hot; apparently, however, their very long continued action is attended with decomposition.

β-Sodium Trimetaphosphimate, $P_3N_3O_6H_2Na_2 + H_2O$.—This form is deposited when the solution has a temperature of 80° or higher. It was obtained

(1) By boiling the solid *α*-salt under a strong solution of sodium nitrite (Anal. 1).

(2) By slowly adding boiling alcohol to a boiling solution of the *α*-salt (Anal. 2).

(3) By pouring a boiling solution of the *α*-salt into a boiling 25 per cent. solution of sodium acetate.

Doubtless other sodium salts would serve equally well, provided their hot solutions are sufficiently strong to throw it out.

The salt lost nothing at 100° and gave:

	Calculated for $P_3N_3O_6H_2Na_2 + H_2O$.	Found. (1)	(2)
P	28.97	28.31	28.97
N	13.11		13.08
Na	21.51	21.86	21.19

(1) P : Na = 3 : 3.12.

(2) P : N : Na = 3 : 2.99 : 2.90.

This modification of the sodium salt forms needles, which, under the microscope, are seen to consist of flat prisms terminating in points; the terminal angles are of two kinds, one rather more, the other rather less than 90°; frequently both

of these may be observed at opposite ends of the same crystal. Often, too, the crystals are cut off obliquely, owing to the development of but one terminal plane, in which case the terminal angles are respectively rather more and rather less than 45°. In general properties it resembles the α-salt, which it gives when reprecipitated from cold solution; whether the difference consists merely in the amount of crystal water, or whether it is a chemically distinct body cannot be decided at present.

Tetra-Sodium Salt, (*Sodium Amido-diimidotriphosphate*), $P_3N_3O_7H_4Na_4 + H_2O$.—As pointed out in the introduction, this is best regarded as the neutral salt of an open chain acid,

$$PO.OH\begin{cases} NH.PO<\begin{matrix} OH \\ NH_2 \end{matrix}, \\ NH.PO(OH)_2 \end{cases}$$

of which trimetaphosphimic acid is the inner anhydride. As positive proof of this cannot be adduced at present, I have preferred to place it among the trimetaphosphimates.

On dissolving sodium trimetaphosphimate in an excess of caustic soda, concentrating and allowing to cool, the salt crystallizes in long brittle needles (Anal. 1). On adding alcohol to a caustic soda solution of sodium trimetaphosphimate (which need not have been heated), it is thrown out as a syrup which crystallizes, slowly if left to itself, at once on adding a fragment of previously prepared salt, to a mass of delicate colorless needles (Anal. 2). These must be washed with alcohol containing a little caustic soda in solution, strongly pressed out and dried out of contact with the air. It contains a large amount of crystal water, which it loses, with the exception of the last molecule, on drying *in vacuo*; the exact amount could not be determined.

The substance dried *in vacuo* lost nothing at 100° and gave:

	Calculated for $P_3N_3O_7H_4Na_4 + H_2O$.	Found. (1)	(2)
P	25.76	25.34	25.60
N	11.66		11.96
Na	25.51	25.60	25.76

(1) P : Na = 3 : 4.08.

(2) P : N : Na = 3 : 3.09 : 4.06.

This salt is very unstable, being decomposed even in the solid state by carbon dioxide. From its cold aqueous solution alcohol precipitates a mixture of unchanged salt and α-sodium trimetaphosphimate, a few reprecipitations converting it completely into the latter and free alkali. Its behavior towards silver nitrate is described under the silver trimetaphosphimates.

Salts with less than three or more than four atoms of sodium could not be obtained.

Potassium Trimetaphosphimate, $P_3N_3O_6H_3K_3$.—A solution of this salt was obtained by decomposing the barium salt with potassium sulphate; on evaporation a transparent, glassy mass resulted. Alcohol precipitated it as a syrup, which, on repeated treatment with absolute alcohol, was converted into indistinct crystals. It was not further examined.

Ammonium Trimetaphosphimate, $P_3N_3O_6H_3(NH_4)_3 + H_2O$. —A solution of this salt was obtained by double decomposition from the barium and silver salts, and by neutralizing the free acid with ammonia. It loses ammonia on evaporation, and leaves a transparent amorphous residue. Its solution, treated with alcohol, gives a deposit of large and beautiful pearly scales, which are characteristic. As these form even in the presence of a large excess of ammonia, it appears that a body analogous to the tetra-sodium salt cannot be thus formed.

The-air dried substance gave:

	Calculated for $P_3N_3O_6H_3(NH_4)_3 + H_2O$.	Found.
P	30.38	30.19
N	27.50	27.03

Magnesium Trimetaphosphimate, $(P_3N_3O_6H_3)_2Mg_3(?)$.—Strong solutions of sodium trimetaphosphimate and magnesium chloride give no precipitate, even on boiling. A solution of the magnesium salt may be obtained by double decomposition. From this alcohol throws down an amorphous flocculent precipitate, and it leaves a soluble transparent residue on evaporating. On boiling the solution is slowly decomposed.

A mixture of a not too dilute solution of sodium salt with

an excess of a strong solution of magnesium acetate remains clear, but is precipitated by acetic acid; on adding a little water this precipitate redissolves, reappears on heating and redissolves on cooling; the nature of these precipitates has not been investigated. With more water the solution remains clear on short boiling, but on continued heating a crystalline precipitate forms, which examination shows to consist of magnesium pyrophosphate and imidodiphosphate, orthophosphoric acid remaining in solution.

The fact that trimetaphosphimic acid is not precipitated in the cold by ammoniacal magnesia mixture affords a valuble means of separating it from some of its decomposition-products.

Barium Trimetaphosphimates.—Much time was spent in studying these salts, until it was found that they are devoid of characteristic properties, and that they are of very varying composition. Both neutral and basic salts exist, and there is a strong tendency to form double salts. The tendency to form complex salts is so strong that when barium nitrate, chloride or acetate is used as the precipitant, the product is invariably contaminated with these. It has proved impossible to obtain a single satisfactory analysis, but the following data may be mentioned:

A salt obtained by decomposing an ethereal solution of phosphorus chloronitride with excess of baryta water consisted of a pulverulent, indistinctly crystalline substance for which the rotio P : Ba = 6 : 4.48 was found, while the calculated ratio for neutral salt is 6 : 3.

The potassium salt, precipitated by ammoniacal barium chloride, gave a preparation in which P : Ba = 6 : 3.68.

Triphosphonitrilic tetrachlorhydrine gave a clear solution with ammonia and barium chloride; on boiling a granular precipitate resulted (Anal. 1).

Ethereal chloronitride and barium acetate solution gave a preparation from which the figures under Anal. 2 were obtained.

A precipitate from the potassium salt and neutral barium chloride gave the results recorded under Anal. (3).

	Calculated for $(P_3N_3O_4H_3)_2Ba_3+4H_2O$.	Calculated for $(P_3N_3O_4H_3)_2Ba_3+6H_2O$.	Found. (1)	(2)	(3)
B	19.89	19.16	19.91	20.86	20.46
Ba	43.96	42.35	41.75	41.91	43.79

(1) P : Ba = 6 : 2.85 ; dried at 100°.

(2) P : Ba = 6 : 2.73 ; dried *in vacuo*.

(3) P : Ba = 6 : 2.91 ; dried at 100°.

The neutral salt is slightly soluble in water and easily in a solution of ammonium chloride ; on boiling the latter it is partially reprecipitated. It also dissolves readily in a strong solution of sodium chloride, and, on warming, the barium sodium salt is precipitated.

Barium Sodium Trimetaphosphimate, $P_3N_3O_4H_3NaBa + 1\frac{1}{2}(?)H_2O$.—This salt is almost insoluble in water, and forms a heavy, crystalline powder, which is seen under the microscope to consist of spherical aggregates with many rhombic facets, or occasionally of single minute crystals, apparently rhombohedra. The ordinary amorphous barium salt is invariably formed by precipitating any soluble trimetaphosphimate with a barium salt *in the cold*, but if the chloride or other salts of sodium be present in sufficient quantity, this passes into the crystalline barium sodium salt, at once on heating, or in the cold after a period varying from a few minutes to several hours. The latter also forms at once on precipitating in hot solutions. It was also obtained by decomposing an etherial solution of chloronitride (1 mol. wt.) with a solution of barium acetate (1 mol. wt.) and sodium acetate (9 mol. wts.). As is so common with salts of barium this tends to "carry down" a considerable amount of the precipitant. A preparation made by the last method mentioned contained 0.49 per cent. chlorine, corresponding to a contamination of 1.44 per cent. barium chloride. After making correction for this the figures under Analysis (3) were obtained, which approximate closely to the theoretical.[1] The excess of barium in Analyses (1) and (2) is accounted for in the same manner. Possibly the difficulty is due to the presence of half dissociated barium ions (*e. g.*,—BaCl) in the solution.

The substance lost but little at 100° and gave :

[1] Richards has pointed out the necessity of making a similar correction in determining sulphuric acid as barium sulphate. Ztschr. anorg. Chem., 8, 413,

	Calculated for $P_3N_3O_4H_3NaBa+1\frac{1}{2}H_2O$.	Found. (1)	(2)	(3)
P	22.09	21.50	21.86	21.99
N	9.99	9.91		
Na	5.47		5.56	5.53
Ba	32.56	35.67	34.22	32.86
H	1.43			1.32

(1) P : N : Ba = 3 : 3.05 : 1.12.
(2) P : Na : Ba = 3 : 1.03 : 1.06.
(3) P : Na : Na : H = 3 : 1.02 : 1.01 : 5.58.

Similar salts containing potassium or ammonium could not be obtained. A barium silver salt consisting of microscopic spherules was obtained by adding silver nitrate to a solution of the neutral barium salt in ammonium nitrate; a qualitative examination showed the presence of barium and silver.

Silver Salts.

Tri-Silver Trimetaphosphimate, $P_3N_3O_4H_3Ag_3$.—This is the most important salt obtained on account of its highly characteristic crystalline form and because it is anhydrous and easily prepared pure, thereby establishing the empirical composition of trimetaphosphimic acid. As those salts which contain crystal water do not lose it completely at a temperature short of decomposition, we should otherwise be unable to decide between the formulas $P_3N_3O_4H_4$ and $P_3N_3O_4H_5$. For comparison the theoretical figures for a silver salt of both of these are given.

The salt may be prepared by precipitating a cold dilute solution (1–50) of the sodium salt by silver nitrate, when it is thrown down at once in the form of colorless elongated microscopic plates, terminated by an angle of 78°. (Analyses 1–4). Much better crystals are obtained if the solution of the sodium salt be acidified with several equivalents of nitric acid and the silver nitrate added slowly, finally in large excess. In this way the crystallization is made to extend over a considerable time, but the precipitation is never complete. (Analysis 5). Thus formed the crystals are usually very well developed, though seldom over 2 mm. long, and consist of thick, monoclinic plates of the forms represented in Figs. 3 and 4, the latter resulting when the crystallization extends over sev-

eral hours. No other faces are ever observed and the angle *a* (between the edges) measured under the microscope, is very nearly 78°.

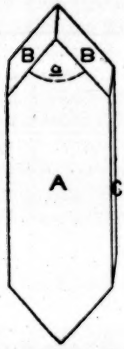


Fig. 3.

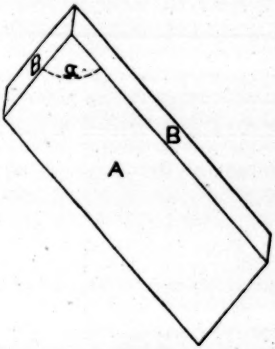


Fig. 4.

$A = \infty P \bar{\infty}$. $B = P \dot{\infty}$. $C = \infty P \dot{\infty}$.

The air-dried salt lost nothing at 100° and gave:

	Calculated for $P_3N_3O_4H_3Ag_3$.	Calculated for $P_3N_3O_7H_3Ag_3$.	Found. (1)	(2)	(3)	(4)	(5)	(6)
P	16.68	16.16	16.50	16.70	16.74	16.64		15.71
N	7.55	7.31		7.53	7.67		7.72	
Ag	58.04	56.20	57.75	57.90	57.77	57.93	57.80	60.08
H	0.54	0.87		0.62				

(1) P : Ag = 3 : 3.02.
(2) P : N : Ag : H = 3 : 2.99 : 2.99 : 3.47.
(3) P : N : Ag = 3 : 2.98 : 3.04.
(4) P : Ag = 3 : 3.
(5) N : Ag = 3 : 3.
(6) P : Ag = 3 : 3.30.

The salt is insoluble in water, easily soluble in ammonia, and somewhat difficultly in dilute nitric acid. It is not affected by light, but on boiling under water it becomes somewhat yellow, owing to the formation of a superficial coating of the six-atom salt and the liberation of free acid, the decomposition-products of which can be detected in the liquid. If

free from silver nitrate, caustic soda does not discolor it, even on boiling. On heating it swells up, gives off ammonia and fuses to a mass which contains metallic silver. In order to ascertain if it is actually precipitated in the anhydrous form, or if it contains water which is given off on standing, a freshly precipitated sample was washed with alcohol and ether, pressed out and at once weighed; it lost nothing at 100°, indicating that even at the moment of formation it is anhydrous. Precipitation from boiling solution seems to have no influence on its composition; if, however, the solution of the sodium salt be added to a large excess of a solution of silver nitrate, the resulting precipitate, though white, is amorphous and contains a much too high percentage of silver (Analysis 6), probably indicating an admixture of a more basic salt.

If tri-silver trimetaphosphimate be heated in a current of dry air at a temperature rising gradually from 200° to 260°, very nearly one-third of the nitrogen is given off as ammonia:

	Calculated for NH_3.	Found.
Loss	3.05	2.86

The product is no longer completely soluble in dilute acid. Alternate treatment with sodium chloride and ammonia extracts the silver and an acid which gives an amorphous precipitate with magnesium nitrate mixture. A considerable white residue remains in the form of pseudomorphs of the original substance, which is insoluble in ammonia, and soluble in hydrochloric acid only on boiling.

Salt with 4 Atoms of Silver, $P_3N_3O_6H_3Ag_4$ or $P_3N_3O_6H_4Ag_4$. —If silver nitrate be added slowly to a solution of the 4-atom sodium salt (sodium amidodiimidotriphosphate) each drop produces a white precipitate, which, on stirring, turns yellowish, in presence of an excess of sodium salt; when the latter is used up and an excess of silver nitrate has been added, it again becomes white. If, on the contrary, the sodium salt be added to the silver nitrate, each drop gives a yellow precipitate, turning white on stirring, and remaining so as long as an excess of silver is present. This white amorphous salt is decomposed by washing with pure water,

turning yellow, while trimetaphosphimic acid goes into solution. The change may be represented thus:

$$3P_3N_3O_7H_4Ag_4 = 2P_3N_3O_7H_3Ag_4 + P_3N_3O_6H_6 + H_2O.$$

Silver nitrate prevents this change; the precipitate must therefore be washed with 1 per cent. aqueous solution of silver nitrate, then with 1 per cent. alcoholic solution of the same, and finally with ether. On pressing out and drying, it then remains colorless. Preparations made in this manner gave the following results after drying at 100°, at which temperature the salt remains white.

	Calculated for $P_3N_3O_6H_3Ag_4$.	Calculated for $P_3N_3O_7H_4Ag_4$.	Found. (1).	(2).	(3).
P	14.01	13.63	13.32	13.70	13.29
Ag	64.92	63.22	65.79	64.71	65.89

(1) P : Ag = 3 : 4.26; (2) P : Ag = 3 : 4.07; P : Ag = 3 : 4.28.

Unfortunately, the figures do not admit of a positive decision as to the formula, but the extreme instability of the salt as compared with the others, may indicate an acid of different nature from trimetaphosphimic acid.

If this salt be allowed to stand for a day or two under pure water, it is converted into a mixture of tertiary silver trimetaphosphimate and a yellow crystalline salt with 6 atoms silver.

$$3P_3N_3O_7H_4Ag_4 = P_3N_3O_7H_3Ag_6 + 2P_3N_3O_6H_3Ag_3 + 2H_2O.$$

The same change occurs rapidly on boiling. Whatever may be the nature of the salt, this change is doubtless due to the tendency of the silver to wander to the nitrogen; silver nitrate, by opposing dissociation, prevents alteration.

Salts with 6 Atoms of Silver, $P_3N_3O_6Ag_6$ and perhaps also $P_3N_3O_7H_3Ag_6$.—Equally unsatisfactory analytical results are given by the salts with 6 atoms of silver. The figures indicate the tendency to formation of salts with the ratio P : Ag = 3 : 6, but the actual ratio only approximates to this, and it is impossible on the basis of the analyses alone to decide which of the formulas $P_3N_3O_6Ag_6$ and $P_3N_3O_7H_3Ag_6$ should be adopted in most cases. After many experiments I have been compelled to abandon for the present the attempt to obtain

these substances in entirely satisfactory condition, and give the figures as actually obtained.

If sodium trimetaphosphimate be added to an excess of an ammoniacal solution of silver nitrate[1] or of a solution of silver oxide in ammonium nitrate,[2] a portion of the trimetaphosphimic acid is precipitated as a pure white voluminous and amorphous body, which, as analysis shows, contains approximately 6 atoms of silver. The precipitation is very incomplete, especially when ammoniacal silver nitrate is used, but in this case the substance contains very nearly 6 atoms of silver, while if the silver oxide solution be employed, the percentage of silver is considerably too low.[3] Heated under the mother-liquor it becomes yellowish, and becomes white again on cooling. After washing out (whereby it becomes yellowish) it dissolves quite readily in strong ammonium nitrate solution, but if boiled with less of the same, or less rapidly if heated with water alone, it is quickly converted into a heavy pulverulent substance. This, if highly magnified, is seen to consist of spherules or indistinct prisms, and has a color varying from orange to deep orange-red, usually the latter. This salt likewise contains 6 atoms of silver. The transformation is prevented by any silver nitrate in the solution, unless the effect of this is neutralized by a large quantity of ammonium nitrate.

If a solution of sodium trimetaphosphimate, to which exactly 3 mol. weights caustic soda, or an excess of ammonia have been added, be dropped into an excess of dilute silver nitrate, a light sulphur-yellow, voluminous and amorphous precipitate is formed, which may be washed with cold water without change, and does not change color on drying. This, likewise, contains 6 atoms of silver, and is *insoluble* in ammonium nitrate. If boiled with a trace of silver nitrate it remains unchanged; but, if boiled with pure water it changes slowly, or if sodium trimetaphosphimate or ammonium nitrate

[1] Prepared by adding ammonia to silver nitrate solution till the brown precipitate just redissolves.

[2] 3 grams silver oxide, 10 grams ammonium nitrate, and 50 cc. water.

[3] The filtrate, on evaporation over sulphuric acid, deposits an imperfectly crystalline substance, at first white, then yellow, which is probably identical with the yellow salt referred to below.

be present, in a few moments, into the same orange-red, crystalline powder above mentioned.[1] On one occasion a deep red crystalline powder was obtained, but the conditions for its formation could not be determined. The following figures resulted from the analyses of these salts, in every case dried at 100°:

	Calculated for $P_3N_3O_7H_2Ag_4$.	Calculated for $P_3N_3O_6Ag_6$.
P	10.39	10.59
Ag	72.21	73.69

White Salt (Amorphous).

	Found. Lowest.	Highest.	Mean.	
P	10.54	11.28	10.92	4 preparations.
Ag	71.04	71.93	71.58	mean ratio P : Ag = 3 : 5.66

Yellow Salt (Amorphous and Crystalline).

P	10.23	10.65	10.44	7 preparations.
Ag	71.55	73.13	72.53	mean ratio P : Ag = 3 : 5.99

Orange-red Salt (Crystalline).

P	10.69	10.91	10.81	5 preparations.
Ag	72.38	72.91	72.61	mean ratio P : Ag = 3 : 5.79

Red Salt (Crystalline).

P	....	....	10.65	1 preparation.
Ag	....	....	73.18	P : Ag = 3 : 5.93

Unsatisfactory as these figures are, they appear to indicate the existence of

(1) A yellow salt, usually amorphous, occasionally crystalline, approximating in composition to $P_3N_3O_7H_2Ag_4$. As this is only formed in the cold from a trimetaphosphimate to which alkali has been added, it may be a salt of the supposed open-chain acid.

(2) A red crystalline salt of the formula $P_3N_3O_6Ag_6$.

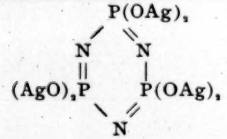
(3) A white amorphous salt of nearly the same composition.

The orange-red salt, invariably containing too little silver, and varying in depth of color, may be a mixture or an intermediate form.

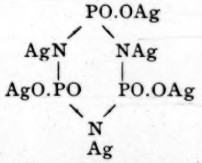
As the white salt is formed only in the presence of silver ammonia compounds, and is quite soluble in ammonium

[1] This is seen to crystallize from the liquid, so that temporary solution must take place.

nitrate, it is clearly different in nature from the others. Probably it contains silver united to oxygen only, while in the red salt one-half the metal is associated with nitrogen. We may regard them as salts of the two forms of trimetaphosphimic acid :



Hexa-silver triphosphonitrilate.



Hexa-silver trimetaphosphimate.

The action of silver nitrate in preventing the transformation may be ascribed to its opposing dissociation. No deep decomposition occurs during the transformation, as the ammoniacal solution is not precipitated by magnesia mixture, and sodium trimetaphosphimate is regenerated by treatment with sodium chloride and acetic acid.

Ferric Trimetaphosphimates.—Gladstone[1] states that when pyrophosphodiamic acid is added to ferric sulphate, acidified with sulphuric acid, a clear solution results, which, on boiling, deposits white ferric pyrophosphamate, which is insoluble in acids but soluble in ammonia. The ferric trimetaphosphimates seem to vary considerably in composition and properties and present no characteristic features. The following points were noted : On adding ferric chloride to a moderately strong solution of sodium trimetaphosphimate an amorphous white precipitate forms which redissolves in an excess of the sodium salt, probably with formation of a ferric-sodium salt, but which becomes permanent on adding more ferric chloride. This is scarcely soluble in dilute hydrochloric acid, but readily soluble in ammonia with faint red color. Sodium hydroxide regenerates sodium salt. If, however, the solution of the sodium salt be dilute, no precipitate forms in the cold, even with an excess of ferric chloride, but on boiling, after acidifying, a white amorphous precipitate is produced, which, like the above, is nearly insoluble in dilute acid and easily

[1] Q. J. Chem. Soc., **3**, 135 : J. Chem. Soc. [2], **2**, 229 ; [2], **4**, 290 ; [2], **6**, 67.

soluble in ammonia and consists of trimetaphosphimate mixed with decomposition products.

The solubility of these salts in ammonia, which they show in common with other ferric amidophosphates and pyrophosphates may be ascribed to the formation of complex ions containing iron, in other words, of *ferri-trimetaphosphimic acids*, analogous to ferri-oxalic acid[1] and similar bodies.

Free Trimetaphosphimic Acid.—Silver trimetaphosphimate, decomposed under cold water by hydrogen sulphide, gives a solution from which, when fresh, the characteristic salts may be prepared, and from which much alcohol gradually throws out an amorphous sticky mass. The solution, on evaporation *in vacuo*, leaves a transparent, gummy residue from which alkalies evolve much ammonia, and which after redissolving, gives a precipitate with magnesium mixture, indicating partial decomposition. The acid seems therefore to be incapable of crystallization.

In marked distinction from metaphosphoric acid, trimetaphosphimic acid does not coagulate albumen.

Decomposition-Products of Trimetaphosphimic Acid.

Orthophosphoric acid and ammonia are the ultimate products of the action of acids on trimetaphosphimic acid, as well as of the decomposition of the free acid alone in aqueous solution when heated or kept for a long time. I have, however, been able to isolate three well marked intermediate bodies, *viz.*,

Diimidotriphosphoric acid, $P_3N_3O_8H_7$;
Imidodiphosphoric acid, $P_2NO_4H_5$;
Pyrophosphoric acid, $P_2O_7H_4$.

If sodium trimetaphosphimate solution (1—15) be boiled with 2–3 mol. weights nitric acid, the transformation into ammonia and orthophosphoric acid is complete in about 10 minutes, but on interrupting the boiling after 3–4 minutes and cooling, the presence of these products can be detected; the same change occurs slowly in the cold, many days being required for complete decomposition. From this solution silver nitrate throws down first the silver salt of unchanged trimetaphosphimic acid, then the others in the order named and finally

[1] See Rosenheim, Ztschr. anorg. Chem., 11, 214, etc.

silver phosphate, which is most easily soluble in nitric acid.

Although these products were first detected in this way, many experiments have convinced me that it is not a practical method of separation. The separation by fractional precipitation is not sharp, the properties of trimetaphosphimic and diimidotriphosphoric acids are so similar and the stability of the latter so slight, that the results are very unsatisfactory. In the absence of trimetaphosphimic acid, however, diimidotriphosphoric acid is readily separated from the later decomposition-products. If, therefore, we have ascertained the time required for all the trimetaphosphimic acid to be decomposed under given conditions, while diimidotriphosphoric acid still remains, we can isolate the latter in a condition of purity. Since the latter is merely a transition-product, the amount present at any time is small, and the actual yield is only about 10 per cent. of the theoretical.

The following method leads to the desired result. 1 mol. weight α-sodium trimetaphosphimate is dissolved in 15 pts. cold water, 3 mol. weights nitric acid (strength about 15 per cent.) added, and the solution allowed to stand for 7 days at the ordinary temperature. Enough ammonia is then added to give a faint odor and an excess of magnesium nitrate mixture[1] added, which throws down imidodiphosphoric, pyrophosphoric and orthophosphoric acids, while diimidotriphosphoric acid remains wholly in solution. The liquid is removed as far as possible from the semi-gelatinous precipitate by suction and pressing out in the filter,[2] without washing. The filtrate is approximately neutralized with nitric acid and precipitated by silver nitrate, a considerable excess of which should be used, as penta-silver diimidotriphosphate is much less soluble in dilute silver nitrate than in water. The slightly washed silver salt still contains some imidodiphosphate, as the magnesium salt of this acid is not wholly insoluble. To remove this it is dissolved in the smallest possible volume and amount of ammonia and a little magnesium nitrate mixture

[1] Made by dissolving 100 grams crystallized magnesium nitrate and 35 grams ammonium nitrate in water, adding enough ammonia to give a faint odor, and diluting to 1 liter.

[2] Schleicher and Schüll's hardened filters, No. 575, have proved indispensable in this operation.

added, which throws out the remaining imido-diphosphoric acid. The liquid is again filtered by suction, with but little washing, and the silver salt again precipitated by neutralizing with nitric acid, with addition of a little silver nitrate. The moist silver salt is treated with an excess of moderately strong solution of sodium chloride, acidified with acetic acid, the silver chloride filtered off with but little washing and an equal volume of alcohol added to the filtrate, which precipitates *tri-sodium diimidotriphosphate*. This is purified by dissolving in a little water and reprecipitating by alcohol.

The magnesium precipitate, containing imidodiphosphoric and a little pyrophosphoric acids, is pressed out strongly under a screw press, pulverized and dissolved in the least possible amount of dilute nitric acid.[1] Ammonia is added drop by drop till a slight *permanent* precipitate forms, and after filtering, silver nitrate added as long as the precipitate is white. Nearly all the orthophosphoric acid remains in solution, even after adding much silver nitrate, but, if too much be added, or if the amount of orthophosphoric acid be relatively great, the latter portions of the precipitate are yellow. Exact quantitative data cannot be given, but in general it is necessary to use an amount of silver nitrate at least ten times the weight of the mixed magnesium salts. Silver pyrophosphate is partly precipitated towards the end, and partly remains in solution. To get rid of it entirely, as well as of traces of orthophosphoric acid and of a substance of relatively high percentage of nitrogen, the tri-silver imidodiphosphate must be dissolved in ammonia, reprecipitated as magnesium salt, pressed out and reconverted into the silver salt in the same manner. The mother-liquor of the second silver precipitation, if neutralized with ammonia, gives a mixture of silver imidodiphosphate and pyrophosphate; this, after conversion into the sodium salt by sodium chloride, addition of a little caustic soda and precipitating by alcohol gives a syrup which is converted by vigorous rubbing into a pasty mass. This, by repeated solution and reprecipitation by alcohol, gives the characteristic flat prisms of sodium

[1] This is best done by rubbing up with water in a glass mortar, adding the acid gradually.

pyrophosphate. After conversion into the silver salt this proved to be free from nitrogen and an analysis gave:

	Calculated for $Ag_4P_2O_7$.	Found.
Ag	71.27	70.23

Tedious as the above method is, many experiments have failed to lead to the discovery of a better one, and have convinced me that it cannot be abbreviated in the least without injuriously affecting the quality of the products.

Diimidotriphosphoric Acid, $P_3N_3O_8H_7$.

This acid forms two series of salts, in which three and five atoms of hydrogen are replaced. The alkali salts with three atoms of metal are of neutral, those with five atoms of alkaline reaction. It seems impossible to replace the two remaining atoms, as is pointed out under the silver salts.

Tri-Sodium Diimidotriphosphate, $P_3N_3O_8H_4Na_3$.—The preparation of this salt is described above. It is easily soluble in water, this solution leaving on evaporation a mass of indistinct prisms. Precipitated from its aqueous solution by alcohol it usually forms granules without evidence of crystalline form, but when very slowly precipitated it may be obtained as flat, very obtusely pointed prisms or rhombic plates, visible only when magnified 400 diameters. It contains no crystal water. The substance dried at 100° gave:

	Calculated for $P_3N_3O_8H_4Na_3$.	Found.
P	28.89	28.73
N	8.72	8.77
Na	21.45	20.69

P : N : Na = 3 : 2.02 : 2.92.

A penta-sodium salt probably exists, being obtained by decomposing the penta-silver salt with sodium chloride. It has alkaline reaction and is precipitated by alcohol as an uncrystallizable syrup.

The tri-sodium salt is not precipitated even in strong solution by magnesium chloride or magnesia mixture unless the latter contains much ammonia; in this case the resulting precipitate is easily soluble in ammonium salts, and hence is probably merely magnesium hydroxide. Barium chloride precipitates from a not too dilute solution microscopic sphe-

rules, which dissolve readily in a cold, strong solution of sodium chloride; on boiling this solution a crystalline precipitate is at once formed, consisting of microscopic rhombohedra (?) resembling sodium barium trimetaphosphimate and probably a double salt.

Silver Salts.—Two of these were obtained, one having the formula $P_3N_3O_6H_4Ag_4$, and the other $P_3O_6O_6H_4Ag_4$. The tendency to formation of the latter is so strong that a solution of the tertiary sodium salt gives with silver nitrate a white amorphous precipitate, which, however, is mixed with some crystals of the former.

Tri-Silver Diimidotriphosphate, $P_3N_3O_6H_4Ag_3$.—This salt is very characteristic. It can be obtained pure only by precipitating an acidified solution of the tertiary sodium salt by an excess of silver nitrate. To a solution of the sodium salt in 30 parts water, 1 to 2 molecular weights nitric acid are added and then silver nitrate gradually; as soon as a milkiness, due to the formation of the penta-salt, is observed, more acid is added, and then more silver nitrate, acid being added as often as necessary; the crystallization soon starts, but several times the theoretical amount of nitrate is required, and under no circumstances is the precipitation complete. Generally spherules with many rhombic facets are obtained, but with slow crystallization (from more dilute solutions) the forms shown in Figs. 5 and 6 result.

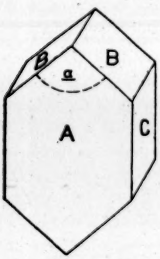


Fig. 5.

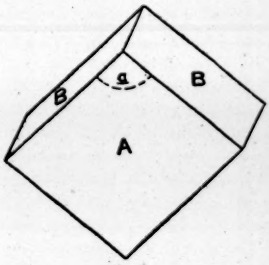


Fig. 6.

$A = \infty P \bar{\infty}$. $B = P \grave{\infty}$. $C = \infty P \grave{\infty}$.

The colorless crystals are monoclinic, and suggest those of tertiary silver trimetaphosphimate, but are shorter and thicker and approach more nearly to the orthorhombic form. No other faces are ever seen. The angle *a* (between the edges), measured under the microscope is very nearly 98°; the acute angle between the edges of B is, roughly speaking, 80°, so that when the form Fig. 6 occurs, and this face is uppermost, it is apt to be mistaken under superficial observation for trimetaphosphimate (angle *a*, 78°).

The salt is practicably insoluble in water, easily in ammonia, and rather difficultly in dilute nitric acid. When pure it is not discolored by light or by caustic soda. It contains no crystal water. Analysis gave:

	Calculated for $P_3N_3O_8H_4Ag_3$.	Found. (1)	(2)
P	16.14	16.39	16.29
N	4.87	4.76	
Ag	56.10	55.94	56.36

(1) P : N : Ag = 3 : 2.01 : 2.94. Direct from decomposed solution of trimetaphosphimic acid.

(2) P : Ag = 3 : 2.99. From sodium salt.

Penta-Silver Diimidotriphosphate, $P_3N_3O_8H_3Ag_5$.—One molecular weight tertiary sodium salt is dissolved with addition of not less than 1½ nor more than 4 molecular weights ammonia, and added to an excess of a solution of silver nitrate; the pure white amorphous voluminous precipitate is washed, sucked out and dried *in vacuo*. When fresh it is colorless, but on drying it assumes a yellowish tint, and after standing for some time it is partially converted into crystals, the nature of which was not determined. On boiling with water it also becomes yellowish, and in each case the change of color is accompanied by decomposition, as its ammoniacal solution is partially precipitated in amorphous form by magnesia mixture, an effect which is not observed in the perfectly fresh white salt. Warming with ammonium nitrate destroys the yellow color, which is consequently not due to silver phosphate. The fact that it remains white on boiling with ammonium nitrate serves to distinguish it from the trimetaphosphimates, the more basic silver salts of which, as pointed out, become

orange-red under these conditions. The salt is very difficultly, yet perceptibly soluble in water, and is reprecipitated by adding considerable silver nitrate; it is easily soluble in ammonia, and nitric acid converts it partly into the tertiary salt before dissolving it.

Dried at 100° it gave :

	Calculated for $P_3N_3O_8H_3Ag_3$.	Found. (1)	(2)	(3)
P	11.77	12.05	11.96	11.75
N	3.55	3.66	3.65	
Ag	68.23	68.96	68.92	69.24

(1) P : N : Ag = 3 : 2.02 : 4.94.
(2) P : N : Ag = 3 : 2.02 : 4.97.
(3) P : Ag = 3 : 5.08.

Attempts to replace one or both of the remaining hydrogen atoms by silver proved unsuccessful. If the tertiary sodium salt be dissolved with 1–2 molecular weights caustic soda, or even with 5–6 molecular weights ammonia, and added to silver nitrate, the resulting precipitate is discolored by free silver oxide. On standing several days it becomes yellow, but its ammoniacal solution is now precipitated by magnesia mixture, indicating decomposition. The magnesia precipitate gave a silver salt resembling tertiary imidodiphosphate, but the exact nature of the decomposition was not investigated.

Imidodiphosphoric Acid, $P_2NO_6H_5$.

This is probably the substance described by Gladstone under the name *pyrophosphamic acid*. It is moderately stable in cold, not too acid, solution, and hence occurs in large amount among the decomposition products of trimetaphosphimic acid.

Trisodium imidodiphosphate, obtained by decomposing the tertiary silver salt by sodium chloride, has alkaline reaction. Its solution, as well as that of the tetra sodium salt, is precipitated by alcohol as a syrup which cannot be made to crystrllize, and the aqueous solution of which dries to a transparent gummy mass. It is more soluble in dilute alcohol than sodium pyrophosphate.

The *magnesium* salt above described is amorphous, volu-

minous, and nearly, but not quite, insoluble in water, and somewhat more soluble in solutions of ammonium salts.

Tri-Silver Imidodiphosphate, $P_2NO_4H_3Ag_3$.—This is obtained as an amorphous, white precipitate, when the free acid, or a solution of a tertiary salt is precipitated by silver nitrate. Thus formed, it tends to collect in small lumps, a property which distinguishes it from any of the other silver salts referred to in this paper. When precipitated by acid from its ammoniacal solution it forms a powder that settles slowly. When slowly separating, or when precipitated from hot solutions, it forms semi-crystalline granules, often united to crusts or dendritic forms. When formed in a moderately acid solution it usually shows a slight deficiency of silver (Anal. 1–2), probably due to a trace of a more acid salt, but such a salt cannot be obtained in pure form. Pure tertiary salt can be obtained by decomposing the crude salt with somewhat less than the required amount of sodium chloride, and reprecipitating. It is insoluble in water and is not affected by light.

Dried at 100° it gave :

	Calculated for $P_2NO_4H_3Ag_3$.	Found. (1).	(2).	(3).	(4).	(5).
P	12.47	13.19	12.75	12.34	12.60	12.19
N	2.82	3.13	3.14	2.86	2.96	2.92
Ag	65.03	63.70	63.87	65.21	65.06	66.46

$$P : N : Ag \begin{cases} (1) = 2 : 1.05 : 2.78; \\ (2) = 2 : 1.09 : 2.78; \\ (3) = 2 : 1.02 : 3.04; \\ (4) = 2 : 1.04 : 2.97; \\ (5) = 2 : 1.06 : 3.14; \end{cases}$$

Tetra-Silver Imidodiphosphate, $P_2NO_4HAg_4$.—This salt exists in a white and in a yellow form. The former is obtained by precipitating a solution of silver oxide in ammonium nitrate by the sodium salt. It forms a voluminous, flocculent precipitate, which remains white only in presence of its mother-liquor; on washing out it undergoes partial transformation into the yellow form, the same change occurring temporarily on boiling under the mother-liquor. It shows a slight deficiency of silver (Anal. 4).

The *yellow* form is obtained as an amorphous, flocculent

precipitate by adding an ammoniacal solution of an imidodiphosphate to an excess of silver nitrate (Anal. 1–2), or as an imperfectly crystalline powder, by evaporating such an ammoniacal solution, containing an excess of silver, over sulphuric acid (Anal. 3). From this it appears that the remaining hydrogen atom is not replaceable by metal. The difference between the white and yellow forms is perhaps due to tautomerism.

Dried at 100°, it gave:

	Calculated for $P_2NO_4HAg_4$.	Found. (1.)	(2.)	(3.)	(4.)
P	10.27	10.17	10.07	....	10.80
N	2.32	2.28	2.45	....	....
Ag	71.39	72.19	72.35	71.01	69.72

(1). P : N : Ag = 2 : 0.99 : 4.01.
(2). P : N : Ag = 2 : 1.07 : 4.13.
(3). P : Ag = 2 : 3.71.

Imidodiphosphoric acid is easily distinguished from diimidotriphosphoric acid by the insolubility of its magnesium salt, by the peculiar granular or lumpy appearance of its tertiary silver salt, by its syrupy tertiary sodium salt, and by its ammoniacal solution giving a yellow salt with silver nitrate, while the silver salt of the latter, found under the same conditions, is either white, or, when too much ammonia has been used, discolored by silver oxide.

Ferric Imidodiphosphate.—No analysis of this was made. It is thrown down on boiling an acidified solution with a ferric salt as a white, amorphous precipitate, difficultly soluble in acids and easily soluble in ammonia.

Cupric Imidodiphosphates.—Several of these appear to exist. The amorphous, light-blue precipitate formed by cupric sulphate in a solution of the sodium salt redissolves in an excess of the latter, but is again reprecipitated by an excess of cupric salt, but under no circumstances completely. It dissolves in caustic potash to a violet solution. The soluble sodium double salt is partially precipitated on heating its aqueous solution, the precipitate redissolving on cooling. The precipitate with excess of cupric sulphate dissolves readily in cold acetic or sulphurous acid, and is tem-

porarily reprecipitated on heating the solution, unless too dilute and too strongly acid, in which case some pyrophosphate crystallizes out on long heating. The same temporary precipitation occurs in a less degree on heating its solution in very dilute nitric acid.

The property of being precipitated from an acid solution on boiling is one which cupric imidodiphosphate shares with the pyrophosphate, and the same is observed with the magnesium salts, but with the difference that the pyrophosphates do not redissolve on cooling, while the imidodiphosphates redissolve either at once or in a short time. It is not possible to effect a complete separation of the two acids in this way, however, for if pyrophosphoric acid be present, more or less imidodiphosphate remains in the permanent precipitate, apparently because of the formation of complex salts containing both acids. The only method for separating the two acids when mixed in approximately equal proportions is to convert them into the sodium salts, and to precipitate repeatedly by alcohol, finally recrystallizing the pyrophosphate from water.

Decomposition of Imidodiphosphoric Acid.—When a soluble imidodiphosphate is boiled with acetic acid, it is converted for the most part into orthophosphoric acid, and to a much less extent into pyrophosphoric acid. The significance of this fact is pointed out in the introduction. A solution of the sodium salt (which analysis has proved to be free from pyrophosphate) in 30–50 parts water is weakly acidified with acetic acid, boiled 7–8 minutes, and cooled. If this solution be made alkaline with caustic soda, and alcohol added, an abundant crystallization of tertiary sodium phosphate is formed, which may be recognized by its crystalline form and by the usual reactions. In this the microscope shows a few crystals of sodium pyrophosphate. The latter acid may be isolated by making use of the fact that a solution of freshly precipitated magnesium pyrophosphate in excess of cold acetic acid is quantitatively precipitated on boiling, in a permanently insoluble form, while magnesium orthophosphate remains dissolved. The above weakly acetic solution is mixed with magnesium acetate in excess, the precipitate dissolved by

adding about one-fifth volume of strong acetic acid, and boiled a few minutes. The precipitated granular magnesium pyrophosphate is dissolved in nitric acid, in the manner described for the separation of the decomposition-products of trimetaphosphimic acid, converted into silver salt and then into sodium salt. This, after several precipitations by alcohol, is recrystallized from water. A careful determination of the yield of pyrophosphoric acid in two experiments gave 13.5 and 16 per cent. of the theoretical. For analysis the sodium salt was converted into silver pyrophosphate, which gave:

	Calculated for $Ag_4P_2O_7$.	Found.
P	10.24	10.35
Ag	71.27	70.74

Decomposition of Sodium Trimetaphosphimate by Acetic Acid.

As before pointed out, this salt is not decomposed by acetic acid in the cold, or on short heating. If, however, its solution is heated for two or three hours with 30 per cent. acetic acid and magnesium acetate, under the conditions mentioned under the magnesium salt, a granular precipitate is obtained, consisting of a mixture or double salt of magnesium pyrophosphate and imidodiphosphate, which does not perceptibly redissolve on cooling, while the liquid contains much orthophosphoric acid. The sodium pyrophosphate, separated from this by the above method, showed the characteristic form. For analysis it was converted into the silver salt, and gave:

	Calculated for $Ag_4P_2O_7$.	Found.
P	10.24	10.43
Ag	71.27	70.33

The following paper will be devoted to the description of *tetrametaphosphimic* acid.

WASHINGTON, D. C., June 30, 1896.

Contributions from the Chemical Laboratory of Harvard College.

XCV.—ON CERTAIN DERIVATIVES OF TRICHLORDINITROBENZOL.

By C. Loring Jackson and W. R. Lamar.

For several years the behavior of various reagents with tribromdinitrobenzol, melting at 192°, has been studied in this laboratory,[1] and, as results accumulated, it became of interest to study the corresponding trichlordinitrobenzol melting at 129°.5, to see whether it behaved in the same way as the bromine compound. This extension of the work was prevented by the extreme difficulty in preparing symmetrical trichlorbenzol by any of the known methods until Victor Meyer and Sudborough published[2] in 1894 their admirable method of preparing trichloraniline, by which it can be made in quantity with no great outlay of time or labor. We have accordingly taken up the study of trichlordinitrobenzol melting at 129°.5, discovered some years ago by J. F. Wing and one of us,[3] and in this paper describe its action with aniline, sodic ethylate, and sodium malonic ester, with the last two of which reagents it behaves in many respects differently from the tribromdinitrobenzol. The behavior of the other reagents with this substance, and a similar study of the trichlortrinitrobenzol will be undertaken in the near future in this laboratory.

When heated with aniline, trichlordinitrobenzol gives the same trianilidodinitrobenzol melting at 179°, which was obtained under the same conditions from tribromdinitrobenzol. With sodic ethylate in the cold tribromdinitrobenzol lost two of its atoms of bromine, which were replaced by two ethoxy radicals forming bromdinitroresorcin diethylether melting at 184°. In just the same way cold sodic ethylate in alcoholic solution converts trichlordinitrobenzol into chlordinitroresorcin diethylether which melts at 160°, but here the resemblance ends, for whereas a hot solution of sodic ethylate replaces the atom of bromine in bromdinitroresorcin diethylether by hydrogen forming dinitroresorcin diethylether melting at 133°, under the same conditions the chlordinitroresorcin diethylether was converted into a mixture of dinitrophloro-

[1] This Journal, 10, 283; 11, 93, 541; 12, 164; 13, 164; 14, 331; 16, 28, 35; 18, 465.
[2] Ber. d. chem. Ges., 27, 3151. [3] This Journal, 9, 348.

glucin triethylether, $C_6H(NO_2)_2(OC_2H_5)_3$, which melts at 104 –105°, and its diethylether, $C_6H(NO_2)_2(OC_2H_5)_2OH$, melting at 166°. The same products were obtained in each case by treating the tribrom- or trichlordinitrobenzol with hot sodic ethylate.

With sodium malonic ester tribromdinitrobenzol gives a rather complex reaction. Two atoms of bromine are removed, one being replaced by the malonic ester radical, and the other by hydrogen, so that the product is bromdinitrophenylmalonic ester, $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$. The trichlordinitrobenzol under the same conditions acts more simply, as only one atom of chlorine is affected, and this is replaced by the malonic ester radical, so that the product is dichlordinitrophenylmalonic ester, $C_6HCl_2(NO_2)_2CH(COOC_2H_5)_2$, which melts at 101°. We have not yet succeeded in replacing one of the atoms of chlorine in this substance by hydrogen under the influence of sodium malonic ester, but hope to try further experiments in this direction. The dichlordinitrophenylmalonic ester resembles the bromdinitrophenylmalonic ester in many of its properties. Both give red sodium salts, and by the action of nitric acid both are converted into nitrites. The nitrite of dichlordinitrophenylmalonic ester has the formula, $C_6HCl_2(NO_2)_2CONO(COOC_2H_5)_2$, and seems to be less stable than the corresponding bromine compound. Both the substituted malonic esters also are saponified by boiling with sulphuric acid of specific gravity 1.44, forming the corresponding phenylacetic acids, but the dichlordinitrophenylacetic acid, $C_6HCl_2(NO_2)_2CH_2COOH$, (melting-point 140°) differs in some striking particulars from the bromdinitrophenylacetic acid. The latter is so unstable that five crystallizations from alcohol are enough to remove carbonic dioxide from it, and convert it completely into bromdinitrotoluol. The same transformation takes place more slowly, when it is crystallized from hot water. The dichlordinitrophenylacetic acid, on the other hand, can be crystallized from hot water without alteration. When it was boiled with alcohol a new compound was formed, but very slowly, so that it was necessary to boil the substance with alcohol for some hours in order to convert it into the new body; this, however, was not the ex-

pected dichlordinitrotoluol, but the ethyl ester of the substituted acetic acid, $C_6HCl_2(NO_2)_2CH_2COOC_2H_5$, which melted at 67–68°. At first we thought that this formation of the ester must have been caused by the presence of a trace of the sulphuric acid used in saponifying the substituted malonic ester, but on repeating the experiment with a sample, which did not contain a trace of sulphuric acid, the same result was obtained. The formation of an ester from an acid and alcohol alone without the aid of a mineral acid has been observed in a few other cases. These are, pyruric acid, described by L. Simon,[1] and also by Emil Fischer and Speier,[2] and tartaric acid described by Berthelot.[3] The easy formation of the ester from our dichlordinitrophenylacetic acid is the less surprising because Victor Meyer[4] and Goldschmidt[5] have recently called attention to the extraordinary ease with which phenylacetic acid itself is converted into its ester.

Another difference between the dichlordinitrophenylacetic acid and the bromdinitrophenylacetic acid appears in their behavior with alkalies. The bromine compound gives an intense dark green coloration with sodic hydrate, whereas the chlorine compound with the same reagent turns crimson at first, but this color fades in a few seconds, and a nearly white salt of the acid is formed. We are of the opinion from these phenomena that both these intense colors are due to compounds similar to those formed by sodic alcoholates or sodic hydrate on trinitrobenzol, studied by Victor Meyer[6] and by Shukoff,[7] on dinitrobenzoic acid studied by Lobry de Bruyn,[8] and later by him and Van Leent,[9] or on bromdinitrobenzoic acid and a number of related substances by Ittner and one of us.[10]

EXPERIMENTAL PART.

Preparation of Trichlordinitrobenzol.

The trichloraniline used in this preparation was made by

[1] Thèses, Paris, 1895. [2] Ber. d. chem. Ges., **28**, 3256.
[3] Ann. de Chim. et de Phys., **68**, 263.
[4] Ber. d. chem. Ges., **28**, 3197. Compare also Shukoff, *ibid*, 3201. [5] *Ibid*, 3224.
[6] *Ibid*, **27**, 3153. [7] *Ibid.*, **28**, 1800.
[8] Rec. Tr. chim. Pays Bas, **14**, 89. [9] *Ibid.*, 150.
[10] *Ibid.*, **28**, 3063. A fuller account of this work, including a study of the product from dinitranisic acid, will appear soon in this JOURNAL.

the excellent method of Victor Meyer and Sudborough[1] as follows: One hundred grams of freshly distilled aniline were dissolved in one kilogram of chloroform, which had been washed to free it from alcohol, and thoroughly dried. The vessel containing this solution was immersed in a bath of ice and water, and dry chlorine passed through the cold liquid, until it was saturated, which occupied from twelve to fifteen hours. It is advisable to introduce the chlorine through a wide tube, as there is danger that a narrow one will be stopped up by precipitated trichloraniline chloride. The precipitate formed by the action of the chlorine was freed from chloroform by means of a filter-pump, dried and washed with water, which removed all the compounds of aniline except the trichloraniline. The yield was good, as 117 grams of trichloraniline were obtained instead of 211 grams, that is 55.4 per cent. of the theoretical amount. The product made in this way was pure enough to be submitted directly to the diazo reaction. It melted at 76° instead of 77°.5. If sufficient care was not taken in washing and drying the chloroform, or if the solution was not cooled during the treatment with chlorine, a more impure product resulted, which it was necessary to purify by distillation.

The trichloraniline was converted into trichlorbenzol as follows: Thirty grams of it were dissolved in 500 cc. of common alcohol and gradually mixed with 17 cc. of strong sulphuric acid (the calculated amount). The liquid was allowed to cool to ordinary temperatures, and then 17 grams of finely powdered sodic nitrite added at one time; after which the mixture was allowed to stand for eight hours. At the end of this time the trichlorbenzol, which had separated, was filtered out and washed with water until free from sodic sulphate. The alcoholic filtrate was then treated with water in the proportion of one volume of water to three volumes of the filtrate, as it had been found that this amount of water precipitated most of the trichlorbenzol, but left the oily impurities in solution. The yield of trichlorbenzol was excellent, 30 grams of trichloraniline gave 25.5 grams of trichlorbenzol

[1] Ber. d. chem. Ges., **27**, 3151.

instead of 27.7 grams, that is 92 per cent. of the theoretical amount.

The trichlorbenzol was converted into trichlordinitrobenzol[1] by dissolving it at ordinary temperatures in nitric acid of specific gravity 1.505, made from nitre and sulphuric acid in the proportion of one molecule of each. After the solid was completely dissolved, it was precipitated by pouring it into cold water, and purified by recrystallization from hot alcohol till it showed the melting-point 129°.5.

Action of Aniline on Trichlordinitrobenzol.

Five grams of trichlordinitrobenzol were mixed with 10.5 grams of aniline, that is a slight excess over the proportion of 6 molecules of aniline to 1 of the trichlordinitrobenzol. The greater part of the solid dissolved in the cold, and the rest went into solution when the mixture was warmed on the steam-bath. The deep-red liquid solidified after it had been heated for an hour on the steam-bath. The solid mass, freed from aniline by treatment with very dilute acid, was recrystallized from alcohol until it showed the constant melting-point, 179°. As this is the melting-point of the trianilidodinitrobenzol, prepared by A. W. Palmer and one of us,[2] by the action of aniline on tribromdinitrobenzol, it seemed unnecessary to submit the substance to analysis. It was obtained in the orange-red prisms described by H. N. Herman and one of us.[3] In this respect, therefore, the trichlordinitrobenzol behaves exactly like the corresponding bromine compound.

Action of Sodic Ethylate on Trichlordinitrobenzol in the Cold.

Ten grams of trichlordinitrobenzol, dissolved in a mixture of 30 cc. of dry benzol and 60 cc. of absolute alcohol, were mixed with the sodic ethylate prepared by treating 2.6 grams of sodium with 65 cc. of absolute alcohol. This gives the proportion of 3 molecules of sodic ethylate to each molecule of trichlordinitrobenzol. The first few drops of the sodic ethylate solution produced a deep wine-red color, but, as more was added, this color grew fainter, fading to a light yellowish red. A considerable evolution of heat was also observed, sufficient to raise the temperature of 155 cc. of the liquid 10°.

[1] This JOURNAL. 9, 348. [2] *Ibid*, 11, 456. [3] *Ibid*, 16, 35.

This is the more remarkable, as no evolution of heat was perceptible in the corresponding reaction of sodic ethylate on tribromdinitrobenzol. In order to make sure that the reaction was complete, the mixture was allowed to stand in a corked flask, at ordinary temperatures, over night, when it was found that a portion of the product had crystallized in clusters of pale yellow needles. The mother-liquor poured off from these crystals was allowed to evaporate spontaneously, and the product of the reaction, after being washed free from sodic chloride with water, was purified by crystallization from hot alcohol, until it showed the constant melting-point, 160°. This substance is the chief product of the reaction; the only other organic product was an oily body which occurred in such small quantity that we were unable to isolate it. The body melting at 160° was dried at 100°, and analyzed with the following result:

0.3192 gram of the substance gave by the method of Carius 0.1600 gram of argentic chloride.

	Calculated for $C_6HCl(OC_2H_5)_2(NO_2)_2$.	Found.
Chlorine	12.22	12.39

The substance is therefore chlordinitroresorcin diethylether, and the action of sodic ethylate on trichlordinitrobenzol is exactly the same as its behavior with tribromdinitrobenzol,[1] which it converts into the bromdinitroresorcin diethylether melting at 184°.

Properties of Chlordinitroresorcin Diethylether.—It crystallizes from alcohol in good sized, yellowish white prisms with square, or nearly square ends, which show a tendency to combine longitudinally, forming twin crystals looking like a grain of wheat, as they taper to fine points at the ends. When crystallized less well it appears in bunches of branching needles. From its solution in benzol it crystallizes in prisms, which effloresce on exposure to the air, and therefore, undoubtedly, contain benzol of crystallization. It melts at 160°. It is practically insoluble in water, whether hot or cold; slightly soluble in ether, carbonic disulphide or cold methyl or ethyl alcohol, much more soluble in hot

[1] Jackson and Warren, This JOURNAL, 13, 164.

alcohol; soluble in benzol, or chloroform; freely soluble in acetone, which is the best solvent for it. The three strong acids have no apparent action on it in the cold, nor is it saponified by cold sodic hydrate.

Action of Hot Sodic Ethylate on Trichlordinitrobenzol.

Ten grams of trichlordinitrobenzol were dissolved in 20 cc. of dry benzol, and this solution, while still warm, was mixed with sodic ethylate prepared by the action of 45 cc. of absolute alcohol on 2.6 grams of sodium. This gave the proportion of 3 molecules of sodic ethylate to each molecule of trichlordinitrobenzol. So much heat was given off on the addition of the sodic ethylate that the liquid began to boil. This violent boiling was checked by cooling the flask with running water, and then the mixture was heated gently on the steam-bath for ten minutes. Longer boiling partially decomposed the first product of the reaction by saponifying one or more of the ethoxy groups which it contained. The best results were obtained with very concentrated solutions, as already described. If more of the solvents was used, it was necessary to heat longer to bring the reaction to an end; for instance, when the mixed liquids amounted to 160 cc. we were obliged to heat them for an hour and a quarter, but in such cases the yield was much less satisfactory than in those where a strong solution was used. During the boiling the same phenomena were observed, which had appeared in the corresponding reaction with tribromdinitrobenzol,[1] that is, the red color of the solution steadily increased in intensity, and an inorganic precipitate (in this case sodic chloride) was formed. A curious odor was also observed in the solution, which was in the case of the bromine compound supposed to accompany the replacement of the halogen by hydrogen, but this supposition was incorrect, as it also appeared in this reaction, where no such replacement took place.

After the boiling was finished the solvents were allowed to evaporate spontaneously, and the residue thoroughly washed with water. The consideration of the organic substance contained in these wash-waters will be postponed to the next

[1] Jackson and Warren, This JOURNAL, 13, 164.

section. The insoluble residue could not be purified by crystallization from alcohol, but by allowing its solution in benzol to evaporate to dryness spontaneously a mixture was obtained of large prismatic crystals and smaller, rather indefinite needles. From this mixture the larger crystals were easily picked out, and these were then purified by recrystallization from alcohol, when they showed the constant melting-point 104–105°. An additional amount of the substance was obtained from an oily product of the reaction, which was found mixed with the original crystals; after standing for three or four weeks it solidified, and was then easily purified by crystallization from alcohol. As the substance gave up its moisture very slowly *in vacuo*, it was dried at about 90°, and then analyzed with the following results:

I. 0.2689 gram of the substance gave on combustion 0.4792 gram of carbonic dioxide and 0.1532 gram of water.

II. 0.3157 gram substance gave 0.5622 gram of carbonic dioxide and 0.1885 gram of water.

III. 0.3316 gram of the substance gave 28.6 cc. of nitrogen at a temperature of 20° and a pressure of 761 mm.

	Calculated for $C_6H(OC_2H_5)_3(NO_2)_2$.	Found. I.	II.	III.
Carbon	48.01	48.60	48.57	
Hydrogen	5.33	6.33	6.63	
Nitrogen	9.34			9.87

These numbers do not agree so closely with those calculated from the formula as could be wished, but we could obtain no better on account of the explosive nature of the substance, which rendered its combustion a matter of great difficulty. In fact, only after several attempts and adopting special precautions, could results as good as these be secured. They are near enough to the theoretical, however, to prove that the substance is the dinitrophloroglucin triethylether, and therefore the reaction has run differently from that observed in the case of hot sodic ethylate and tribromdinitrobenzol, as then one of the atoms of bromine was replaced by hydrogen giving dinitroresorcin diethylether.

Properties of Dinitrophloroglucin Triethylether, $C_6H(NO_2)_2(OC_2H_5)_3$.—This substance crystallizes from benzol at first

in rhombic plates, but, as the crystallization continues, the acute angles of these plates become more and more strongly truncated, until the plates develop into prisms terminated at each end by two planes at an obtuse angle to each other. These crystals are frequently more than a centimeter long and somewhat less than a centimeter broad. They have a yellowish color and turn dark brown on exposure to the air and light, a change which takes place more rapidly when they are heated to 100°. They melt at 104–105°. They are very freely soluble in alcohol; freely soluble in glacial acetic acid, chloroform, or benzol; soluble in ether, slightly soluble in carbonic disulphide, or in cold methyl or ethyl alcohol, but freely soluble in the two alcohols when they are hot; essentially insoluble in ligroïn, or in water even when hot. The best solvent for it is hot alcohol, or benzol. It dissolves in cold strong sulphuric acid with a yellowish brown color, and water seems to precipitate it unaltered from this solution. It appears to be insoluble, or nearly so, in cold strong nitric acid, but dissolves readily when heated with it. This solution, on cooling, deposits long, slender, pale-yellow crystals, which have not yet been examined more carefully. Strong hydrochloric acid does not act on it in the cold, or even when heated to 100° in a sealed tube with it, but if the temperature is raised to 150°, the ether is saponified, as is shown by the evolution of a gas burning with a green-bordered flame, when the tube is opened, which is undoubtedly ethyl chloride. The other product of the reaction is principally dissolved in the liquid to which it imparts a deep brown-red color. Want of time has prevented us from preparing it in quantity for analysis. It seemed to be a yellow phenol, which sublimed with difficulty. Sodic hydrate, even in boiling solution, acted only slowly and incompletely on the dinitrophloroglucin triethylether, forming a brownish-red solution of the sodium salt of a phenol soluble in water or salt solutions.

Dinitrophloroglucin Diethylether, $C_6H(NO_2)_2(OC_2H_5)_2OH$.

The sodium salt of this substance was formed by the action, already described, of hot sodic ethylate on trichlordinitrobenzol, and was dissolved in the water, with which the

original product was washed. It was obtained by acidifying these wash-waters with hydrochloric acid and recrystallizing the dark-brown precipitate from alcohol, till it showed the constant melting-point, 166°. The longer the mixture of trichlordinitrobenzol and sodic ethylate was heated, the larger was the proportion of diethylether formed, which renders it probable that the triethylether is the first product of the action, and that the diethylether is formed from it by a subsequent reaction. The same substance was the principal product when chlordinitroresorcin diethylether was treated with a hot solution of sodic ethylate. It was mixed in this case with a little of the dinitrophloroglucin triethylether just described.

The substance was dried at 100° and analyzed. The results obtained agreed with the numbers calculated for dinitrophloroglucin diethylether better than with anything else, but the agreement was not close enough to make it worth while to publish them. These variations are undoubtedly due to the fact that the substance is very explosive, since these analyses were made with only the ordinary precautions. We have not repeated the combustions under more carefully regulated conditions, because the analyses given below of the salt of this substance establish its composition sufficiently.

Sodium Salt of Dinitrophloroglucin Diethylether,

$C_6H(NO_2)_2(OC_2H_5)_2ONa.2H_2O$.

This salt was made as follows: A quantity of the dinitrophloroglucin diethylether was treated with a solution of sodic hydrate (made from sodium) in quantity insufficient to convert the whole of it into the salt. The dark orange-red solution thus obtained was filtered from the unchanged phenol, concentrated, and then allowed to evaporate spontaneously. The salt thus prepared gave the following results on analysis:

I. 0.5122 gram of the air-dried salt lost, when dried at 100°, 0.0571 gram of water.

II. 0.6242 gram of the salt lost 0.0688 gram of water.

	Calculated for $C_6H(NO_2)_2(OC_2H_5)_2ONa.2H_2O$.	Found. I.	II.
Water	10.91	11.14	11.02

I. 0.4551 gram of the salt dried at 100° gave 0.1100 gram of sodic sulphate.

II. 0.5554 gram of the salt dried at 100° gave 0.1336 gram of sodic sulphate.

	Calculated for $C_6H(NO_2)_2(OC_2H_5)_2ONa$.	Found. I.	II.
Sodium	7.82	7.83	7.79

In making these analyses it was necessary to apply the heat at first with the greatest care, for, if the temperature rose too high before the phenol was decomposed, an explosion took place.

Properties of the Sodium Salt of Dinitrophloroglucin Diethylether. — Crystallized from water it forms good-sized flat prisms either with square ends or terminated by two planes at an obtuse angle, which is sometimes truncated, or even cut off by a number of smaller modifications. It has a brownish-orange color, and when heated to 135° for some time is partially decomposed with the formation of a slight orange sublimate. Its aqueous solution is dark orange red and gives a neutral reaction. It gave striking precipitates with the following reagents:

With salts of *calcium*, *strontium* or *barium* a bright yellow, gelatinous precipitate, if the solution was concentrated.

With *ferric chloride* salmon-colored flocks.

With *plumbic acetate* yellow flocks.

With *mercuric chloride* yellow flocks, but in smaller quantity than with a salt of lead.

Properties of Dinitrophloroglucin Diethylether.—This substance crystallizes from alcohol in sharp, yellowish-white needles. It melts at 166°, and sublimes although very slowly even at 135°. It is very soluble in acetone or chloroform; soluble in benzol, ether, glacial acetic acid or carbonic disulphide; more soluble in methyl than in ethyl alcohol; slightly soluble in hot water, but practically insoluble in cold; essentially insoluble in ligroïn. Alcohol is the best solvent for it. Apparently unaffected by strong hydrochloric acid in the cold; very slightly, if at all, soluble in cold nitric acid, but dissolves when heated with it; cold strong sulphuric acid dis-

solves it, forming a yellow liquid. Sodic hydrate converts it into the salt already described.

Action of Sodium Malonic Ester on Trichlordinitrobenzol.— Thirty grams of trichlordinitrobenzol (melting at 129°.5) dissolved in 60 cc. of benzol, were mixed with 35.6 grams of malonic ester, previously converted into the sodium salt by treatment with the sodic ethylate made from 5 grams of sodium and 200 cc. of absolute alcohol. These proportions give three molecules of the ester for each molecule of trichlordinitrobenzol. The mixture was allowed to stand at ordinary temperatures in a corked flask for twenty hours and then the dark-red liquid poured into five times its volume of cold water acidified with dilute sulphuric acid, and allowed to stand till the next day. During this second standing the portion of the product which had been precipitated in the aqueous solution, was converted from an oily to a crystalline consistency, and could then be filtered out without difficulty. The larger part of the product, however, was not here, but was dissolved in the benzol, which collected on the bottom of the beaker. This was separated, and mixed with hot alcohol, from which crystals were deposited as the mixture cooled. These crystals and those obtained from the aqueous liquid were purified by crystallization from hot alcohol, until they showed the constant melting-point 101°, when the substance was dried *in vacuo* and analyzed with the following results:

I. 0.3006 gram of the substance gave on combustion 0.4400 gram of carbon dioxide and 0.0866 gram of water.

II. 0.2223 gram of the substance gave by the method of Carius 0.1625 gram of argentic chloride.

III. 0.2411 gram of the substance gave 0.1757 gram of argentic chloride.

	Calculated for $C_6H(NO_2)_2Cl_2CH(COOC_2H_5)_2$.	Found.	
	I.	II.	III.
Carbon	39.50	39.92	
Hydrogen	3.04	3.20	
Chlorine	17.97	18.08	18.02

The substance, like those already mentioned in this paper, is very explosive, so that a good combustion could be obtained only by special precautions, such as mixing the sub-

stance with a large quantity of the powdered cupric oxide in a bayonet tube, or using a long copper boat in which the substance was mixed with much powdered cupric oxide, and the successive portions of it separated by dams of the pure oxide. In any case the heat must be applied with the greatest caution. Even with these precautions we did not succeed in getting satisfactory nitrogen determinations, the numbers coming more than one per cent. too high. This we ascribe to the presence of a combustible gas driven over the cupric oxide so rapidly by the explosive burning of the substance that it escaped combustion. We should not mention this observation if it had not been made in other cases during the determination of nitrogen in ethyl esters. The analyses given above show that the substance is the dichlordinitrophenylmalonic ester, formed by the replacement of one atom of chlorine by one malonic ester radical. The action of sodium malonic ester upon trichlordinitrobenzol is different from its behavior with the corresponding bromine compound, as in that case not only is one atom of bromine replaced by the malonic ester radical, but another is replaced by hydrogen, so that the product is the bromdinitrophenylmalonic ester, $C_6H_3(NO_2)_2BrCH(COOC_2H_5)_2$.

The yield of the dichlordinitrophenylmalonic ester is satisfactory. We obtained from 30 grams of trichlordinitrobenzol 23.8 grams of the ester instead of the 43.6 grams calculated from the reaction, that is 54.5 per cent. of the theoretical yield. The real yield is even somewhat better than this, as a certain amount of unaltered trichlordinitrobenzol was usually detected in the mother-liquors. It was not present, however, in sufficient quantity to make it worth while to recover it.

Properties of Dichlordinitrophenylmalonic Ester.—When crystallized from alcohol it forms thick, narrow plates terminated by two planes at an acute angle to each other. Crystallized from benzol or chloroform it appears in stellate groups of small needles. It is white with a slight pearly luster, and melts at 101°. It shows a marked tendency to explode. It is freely soluble in benzol, chloroform or acetone; soluble in alcohol, ether or glacial acetic acid; slightly soluble in carbonic disulphide or ligroïn; essentially insoluble in water.

The best solvent for it is alcohol. It is insoluble in strong hydrochloric acid, whether hot or cold; slightly soluble in hot sulphuric acid diluted with its own volume of water when heated with it, but this solution is accompanied by saponification, as described later in this paper; insoluble in hot, strong nitric acid, but converted by it into the nitrite described in the next section. Sodic hydrate dissolves it, forming a red solution, and we hoped by this action to get the red salt of the dichlordinitrophenylmalonic ester, but found that the sodic chloride was formed, whether the sodic hydrate was used in aqueous or alcoholic solution, and this even when the ester was in considerable excess. From some preliminary analyses we should judge that one atom of chlorine was removed, but the careful study of this reaction must be postponed for the present.

The Nitrite of Dichlordinitrophenylmalonic Ester, $C_6HCl_2(NO_2)_2CNO_2(COOC_2H_5)_2$.—This substance was made as follows: Two grams of dichlordinitrophenylmalonic ester were warmed on the steam-bath with 7 grams of nitric acid (sp. gr. 1.38) for five minutes. The ester did not dissolve, but melted to an oily drop, which as the heating continued took on an amber color, while at the same time an evolution of gas was observed. After the heating was finished, the liquid was allowed to cool and then poured into about three times its volume of cold water, with which it was thoroughly stirred and allowed to stand until the oily particles had settled, when the supernatant liquid was decanted and the oil washed till free from acid. During this washing the oil was frequently stirred under water with a sharp glass rod, when it usually solidified in the course of half an hour. The substance should be brought into the solid state before dissolving it for crystallization, as if this precaution is neglected, after solution and evaporation of the solvent it shows a tendency obstinately to remain liquid. It was purified by crystallization from alcohol, dried and analyzed with the following result:

0.2905 gram of the substance gave by the method of Carius 0.1873 gram of argentic chloride.

	Calculated for $C_6HCl_2(NO_2)_2CNO_2(COOC_2H_5)_2$.	Found.
Chlorine	16.14	15.94

The substance therefore is a nitrite exactly similar to that obtained under the same conditions from the bromdinitrophenylmalonic ester.[1] The yield is essentially quantitative. Two grams of the ester gave 2.2 grams of the nitrite instead of the 2.23 grams required by the theory, that is a yield of 99 per cent.

Properties of the Nitrite of Dichlordinitrophenylmalonic Ester.—When crystallized by spontaneous evaporation from a cold, saturated, alcoholic solution, it forms glistening, compact, white crystals often a millimeter or more in diameter, which seem to be more or less distorted octahedra. It has no definite melting-point, as different portions of the same specimen melted at 87°–89°, if heated very slowly, or at 94°–95°, if heated more rapidly. It seems to be a decomposition rather than a fusion. It is freely soluble in ether, benzol, chloroform, acetone or carbonic disulphide; soluble in methyl alcohol, and somewhat more freely so in ethyl alcohol; moderately soluble in glacial acetic acid; slightly soluble in hot ligroïn; essentially insoluble in cold ligroïn, or in water either cold or hot. Alcohol is the best solvent for it; from benzol, ether, or chloroform we could not succeed in getting it in a crystalline state. It is insoluble in strong hydrochloric acid whether cold or hot; cold strong sulphuric acid does not dissolve it, but when hot a brown solution is formed. A solution of sodic hydrate does not affect it in the cold, but if the mixture be heated, the nitrite at first melts to a bright red oil and then slowly goes into solution. The reddish-yellow liquid thus obtained gives no precipitate when acidified with dilute nitric acid, but the acid liquid gives a strong test for a chloride showing that the solution of the nitrite in the sodic hydrate has been attended with a deep-seated decomposition. Ammonic hydrate has no effect on the nitrite in the cold, and but little when hot, for although the aqueous solution took on a yellowish tinge, the greater part of the nitrite was recovered unaltered, as shown by its decomposition-point 87°–89°. No

[1] This JOURNAL, 14, 331.

test for a chloride could be obtained in the acidified aqueous solution.

When the nitrite mixed with a slight excess of aniline was gently heated on the steam-bath, it went into solution, and then after heating for ten or fifteen minutes, became nearly solid. After removing the excess of aniline by washing with acidified water, a substance was obtained which crystallized from a mixture of chloroform and alcohol in a mat of white slender needles which did not melt at 340°, and gave no test for chlorine with a copper wire. The acid wash-waters gave a strong test for chlorides. Lack of time has prevented us from studying this substance.

Action of Aniline on Dichlordinitrophenylmalonic Ester.

Aniline did not react on the ester in the cold. If the two substances were heated for about an hour on the steam-bath a red color appeared, but most of the ester was recovered unaltered. When they were heated in an oil-bath to 150°–160° for ten minutes, a reaction took place, as was shown by the formation of aniline chloride, and the other product of the reaction was a red viscous body, which hardened to a varnish on long standing. We have not succeeded in bringing this substance into a crystalline state by any means we could devise, and therefore have not attempted to analyze it. This is the more strange as the anilidodinitrophenylmalonic ester is a well crystallized substance.

Saponification of Dichlordinitrophenylmalonic Ester.

Five grams of the ester (melting-point 101°) were boiled under a return-condenser with 500 cc. of sulphuric acid of specific gravity 1.44, as this strength of acid had given excellent results in many other cases. The ester at first melted, and floated in yellowish oily drops on the surface of the acid, but as the reaction went on a large part of it dissolved in the acid, imparting to it a pale-yellowish color. With the amount of acid used the whole of the organic substance did not go into solution, but as the original ester was replaced by the saponification-product, the drops sank to the bottom of the flask. It was necessary to boil the mixture for three or four hours to obtain complete saponification. At the end of this

time the solution was allowed to cool, when the product crystallized out, and was easily purified by one recrystallization from water acidified with a little sulphuric acid. It then melted constant at 140°. Alcohol should not be used in purifying it, as this acts upon it in a way to be described later. A small additional amount of the substance can be obtained by concentrating the acid liquid from which the original crystals were filtered out. The substance was dried at 100° and analyzed with the following result:

I. 0.1463 gram of the substance gave by the method of Carius 0.1419 gram of argentic chloride.

II. 0.2342 gram of the substance gave 19.5 cc. of nitrogen at a temperature of 23° and a pressure of 765.9 mm.

	Calculated for $C_6HCl_2(NO_2)_2CH_2COOH$.	Found. I.	II.
Chlorine	24.07	23.98	
Nitrogen	9.49		9.46

The substance is therefore dichlordinitrophenylacetic acid, and the saponification is exactly similar to that of the bromdinitrophenylmalonic ester.

The yield is not far from quantitative. 5 grams of dichlordinitrophenylmalonic ester gave 3.4 grams of the substituted acetic acid instead of the 3.7 grams required by the reaction, that is, 91 per cent. of the theoretical yield.

The following observation throws some light on the manner in which the saponification takes place. The crude product resulting from an experiment like that described above was mixed with aqueous ammonic hydrate and warmed gently on the steam-bath. About half of the solid went into solution, and this solution, after being freed from the undissolved portion by filtration, gave a precipitate on the addition of nitric acid, which was recognized as dichlordinitrophenylacetic acid by its crystalline form and its constant melting-point, 140°. The undissolved portion, after recrystallization from alcohol, showed the constant melting-point, 67–68°, and was therefore the dichlordinitrophenylacetic ester described later in this paper. From this it follows that one of the two carboxethyl groups ($COOC_2H_5$), in the malonic ester is saponified, and then loses carbonic dioxide before the second carboxethyl group is affected by the acid.

An attempt was also made to saponify the dichlordinitrophenylmalonic ester with a weaker sulphuric acid, in the hope that a different saponification-product might be obtained. The acid used in this case had a specific gravity of 1.195, and therefore contained 25 per cent. of sulphuric acid; the product, however, was the same as before, that is, the dichlordinitrophenylacetic acid, which was recognized by its melting-point, 140°.

Properties of Dichlordinitrophenylacetic Acid, $C_6HCl_2(NO_2)_2CH_2COOH$.—This substance crystallizes from acidified water in clusters of yellowish-white needles often 2 to 3 centimeters long, which show a tendency to twin longitudinally. The crystals are also sometimes arranged in pinnately branching groups, or in forms like a short bushy tree, tapering to a sharp point. It melts at 140°. It is very soluble in glacial acetic acid, or acetone, but is deposited as a white varnish from these solutions; soluble in benzol or chloroform; moderately soluble in ether; practically insoluble in carbonic disulphide, or in ligroïn, hot or cold. It is freely soluble in methyl or ethyl alcohol, but the substance is affected by the alcohol in a way which will be described later. Nearly insoluble in cold water, slightly soluble in boiling water, and this solubility is much increased by the presence of a small amount of sulphuric acid. Water containing some sulphuric acid is the best solvent for it. Neither hydrochloric acid nor nitric acid dissolves it.

An aqueous solution of sodic hydrate dissolves the dichlordinitrophenylacetic acid forming a beautiful crimson liquid, which loses this color almost immediately. With an alcoholic solution of sodic ethylate the same color is obtained, but in this case it is much more permanent, lasting for as much as twenty-five minutes. The addition of water discharges the color instantly. This crimson color is undoubtedly analogous to the colors obtained by the action of sodic hydrate or ethylate on various nitro compounds and studied by Victor Meyer,[1] Lobry deBruyn and Van Leent,[2] and Jackson and Ittner.[3] We are led to this conclusion by the transitory nature

[1] Ber. d. chem. Ges., **27**, 3153. [2] Rec. Trav. chim. Pays Bas, **14**, 150.
[3] Ber. d. chem. Ges., **28**, 3063.

of the color, and by the fact that the sodium salt of the dichlordinitrophenylacetic acid (which is described later) is nearly colorless. It is probable that the dark Prussian green color obtained by the action of sodic hydrate on bromdinitrophenylacetic acid[1] is also due to a substance of this class and not the salt of the acid as was supposed when it was described. Ammonic hydrate dissolves the dichlordinitrophenylacetic acid giving a greenish-yellow solution, which after acidification with nitric acid gave no test for a chloride.

Sodium Salt of Dichlordinitrophenylacetic Acid,
$C_6HCl_2(NO_2)_2CH_2COONa$.

The salt was made by boiling an aqueous solution of sodic carbonate with an excess of the acid, and filtering out the unaltered acid from the cold solution, which was then concentrated and set aside to crystallize spontaneously. The crystals dried at 100° were analyzed with the following result:

0.1965 gram of the salt gave 0.0436 gram of sodic sulphate.

	Calculated for $C_6HCl_2(NO_2)_2CH_2COONa$.	Found.
Sodium	7.25	7.19

The salt has a pale yellow color and is crystalline. When the powdered salt is brought in contact with water it seems at first to swell, and then dissolves to a pale yellow, neutral liquid. This aqueous solution of the salt gives the following precipitates:

With *ferric chloride* a white flocculent precipitate.

With *cupric sulphate* a greenish-blue precipitate.

With *plumbic acetate* a white curdy precipitate.

With *argentic nitrate* a bluish-white, translucent, gelatinous precipitate.

No precipitates were observed with most of the other common reagents.

Action of Alcohol on Dichlordinitrophenylacetic Acid.

As has been mentioned already the dichlordinitrophenylacetic acid is acted on by alcohol with the formation of a new substance, as was indicated by the fact that the melting-point was lowered several degrees by a single crystallization from

[1] Jackson and Robinson, This JOURNAL, 11, 541.

this solvent. As this action was not very rapid, we boiled some of the compound with alcohol in a flask with a return-condenser for fifteen hours. At the end of this time the alcohol was allowed to evaporate spontaneously, when the product of the reaction was left as a yellowish varnish. After trying in vain to crystallize this from the commoner solvents, we proceeded as follows: The substance was extracted several times with boiling water containing a little sulphuric acid to remove any of the unaltered acetic acid, and then the residue was dissolved in boiling ligroïn, from which it crystallized on cooling. After this there was no difficulty in recrystallizing it from alcohol. When it had reached the constant melting-point, 67–68°, it was dried *in vacuo* and analyzed with the following results:

I. 0.1596 gram of the substance gave on combustion 0.2195 gram of carbonic dioxide and 0.0463 gram of water.

II. 0.2524 gram of the substance gave by the method of Carius 0.2239 gram of argentic chloride.

III. 0.2950 gram of the substance gave 0.2607 gram of argentic chloride.

IV. 0.2086 gram of the substance gave 0.1856 gram of argentic chloride.

	Calculated for $C_6HCl_2(NO_2)_2CH_2COOC_2H_5$.	Found.			
		I.	II.	III.	IV.
Carbon	37.15	37.50			
Hydrogen	2.48	3.22			
Chlorine	21.98		21.94	21.85	22.00

The poor results obtained from the combustion are due to the explosive nature of the substance. These numbers show that the substance is the dichlordinitrophenylacetic ester, and, therefore, that the reaction is different from that with brom-dinitrophenylacetic acid, which is converted by boiling alcohol into the corresponding toluol. In view of this difference, we thought it well to confirm our analyses by preparing the ethyl ester in the usual way. Accordingly, 1 gram of the dichlordinitrophenylacetic acid was dissolved in 10 cc. of absolute alcohol and the solution saturated with dry hydrochloric acid gas. The alcohol was then allowed to evaporate spontaneously, when the ester was left in crystals, which,

after being washed free from hydrochloric acid, melted at 67–68°, and were therefore identical with those obtained by the action of hot alcohol.

The formation of the ester from dichlordinitrophenylacetic acid and alcohol alone seemed so strange that we were inclined to ascribe the action to the presence of a trace of sulphuric acid remaining from the acidified water used in crystallizing the acid. To settle this point a specimen of the dichlordinitrophenylacetic acid was recrystallized from boiling water and thoroughly washed. It melted at the right point, 140°, and gave no test for sulphuric acid. It was boiled for several hours with alcohol in a flask fitted with a return-condenser, and, after the alcohol had been evaporated off, extracted repeatedly with boiling water, and then crystallized from ligroïn, when the ester was obtained as shown by the melting-point, 67–68°. This experiment proves that dichlordinitrophenylacetic acid is converted into its ester by alcohol alone without the aid of any mineral acid. In this connection it should be mentioned that several chemists[1] have recently called attention to the great ease with which phenylacetic acid is converted into its ester. None of them, however, seemed to have tried the experiment without the help of a mineral acid. It will be interesting to determine in this way whether phenylacetic acid can be esterified by alcohol alone, or whether our body owes this property to the presence of the negative radicals attached to the benzol ring.

Properties of Dichlordinitrophenylacetic Ethyl Ester, $C_6HCl_2(NO_2)_2CH_2COOC_2H_5$.—The substance crystallizes from alcohol in rather long white needles with nearly, but not quite, square ends. It melts at 67–68°. It is very soluble in ether or acetone; freely soluble in benzol, carbonic disulphide, or chloroform; soluble in glacial acetic acid. From these solvents it is deposited as a varnish. Soluble in methyl or ethyl alcohol; very slightly soluble in cold ligroïn, more soluble in hot, but not freely even in this; essentially insoluble in water, hot or cold. The best solvents for it are alcohol, or hot ligroïn. It is insoluble in strong nitric acid, or in hydrochlo-

[1] Victor Meyer, Ber. d. chem. Ges., **28**, 3197; Shukoff, *Ibid*, 3201; Goldschmidt, *Ibid*, 3224.

ric acid. With an alcoholic solution of sodic hydrate or sodic ethylate it gave a crimson color, undoubtedly due to a compound similar to that produced by the action of the same reagents on the acid. With aqueous sodic hydrate and a little alcohol it was saponified when heated, but apparently at the same time a portion of the chlorine it contained was removed. We had not time to give this reaction the study it deserves.

The study of these compounds and of the behavior of trichlordinitrobenzol with other reagents will be continued in this laboratory.

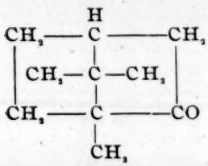
Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XIII.—CAMPHORIC ACID.

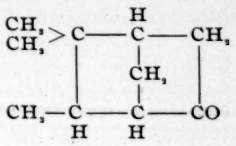
FOURTH PAPER.

By W. A. Noyes.

The formula for camphor, which appears at the present time, to be most in favor, is that of Bredt.[1] A formula more recently proposed by Tiemann[2] does not appear to have been as well received, though he appears to consider that the work done in his laboratory furnishes complete proof that it is correct. These formulæ are as follows:



Bredt.



Tiemann.

Each of these formulæ supposes camphoric acid to be a derivative of glutaric acid. In my last paper[3] several reasons, which appeared conclusive, were given for believing that camphoric acid is a derivative of succinic rather than of glutaric acid. This opinion has received additional support from the work to be described in this paper, and it would seem that Bredt's formula can no longer be considered a possible ex-

[1] Ber. d. chem. Ges., **26**, 3047. [2] *Ibid.*, **28**, 1087.
[3] This Journal, **17**, 421.

pression for the structure of camphor. The same line of work which proves the falsity of Bredt's formula, also renders Tiemann's equally untenable. In addition to this, it was pointed out in my last paper[1] that dihydrohydroxycampholytic acid conducts itself in such a manner toward Beckmann's chromic acid mixture as to indicate that the hydroxyl which it contains is tertiary. If this view is correct, the carboxyl of aminolauronic acid must also be tertiary, while that of dihydroaminocampholytic acid, according to the experiments of Walker[2] and myself[3] is secondary. There should, therefore, in accordance with the well-known laws of esterification for secondary and tertiary carboxyl, be a marked difference in the rate of esterification for the two acids. According to Tiemann's formula, however, the rate of esterification for the two acids should be practically identical.

The experiment was tried as follows: A mixture of 10 grams of dihydroaminocampholytic acid, 40 cc. of absolute alcohol and 3 cc. of concentrated sulphuric acid was boiled with a reversed condenser for three hours. A part of the alcohol was then distilled off, the residue was diluted, rendered alkaline with sodium hydroxide, and the ester formed taken up with ether. After distilling off the ether, the ester, which is a strong base, was titrated with dilute sulphuric acid. The amount of ester formed was 5.2 grams. 11 grams of the chloride of aminolauronic acid, treated in exactly the same manner, gave only 0.48 gram of the ester. More than ten times as much of the first acid, therefore, was converted into the ester. The result conclusively disproves Tiemann's formula, while it is in entire accord with the conclusion reached by Walker and myself. It would also agree with Bredt's formula.

Ethyl Ester of Aminolauronic Acid.

When mixtures of the proportions given above are boiled for two or three days, about thirty per cent. of the aminolauronic acid is converted into the ethyl ester. The free ester is a mobile, strongly basic liquid with an ammoniacal, aromatic odor. On neutralizing the ester with sulphuric acid of

[1] *Loc. cit.*, p. 426. [2] J. Chem. Soc., **63**, 506, (1893).
[3] This JOURNAL, **16**, 509; and **17**, 421.

25 per cent. a considerable part of the *sulphate* formed separates in difficultly soluble, pearly-white scales.

0.1432 gram of the sulphate gave 0.0663 gram $BaSO_4$.

	Calculated for $(C_8H_{14}{<}^{NH_2}_{CO_2C_3H_8})_2H_2SO_4$.	Found.
S	6.45	6.38

Hydroxylauronic Acid.

The fact that the treatment of aminolauronic acid with nitrous acid[1] gives rise to the formation, along with other products, of isocampholactone, and that no other hydroxy acid could be found among the products of decomposition, would, in the absence of evidence to the contrary, indicate that the amino group is in the γ-position with reference to the carboxyl. While the evidence given in my last paper furnishes satisfactory reasons for believing that the hydroxyl group of the acid corresponding to the lactone is combined with a different carbon atom from that with which the amino group of aminolauronic acid is combined, the preparation of the hydroxy acid corresponding to the latter was of very considerable interest. This has now been effected. When the neutral sulphate of the ester of aminolauronic acid is treated with a strong solution of sodium nitrite it is decomposed with the formation, chiefly, of the ethyl ester of γ-lauronolic acid,[2] (the allo-campholytic acid of Walker[3]) together with a small amount of the ethyl ester of the new hydroxylauronic acid. The two esters may be partly separated by fractional distillation under diminished pressure, but the complete separation of the two acids is best effected, after saponifying the esters with alcoholic potash, and taking up the acids from the acidified solution with ether, by distilling with water-vapor. The hydroxy acid is almost non-volatile and by continuing the current of steam for some time the γ-lauronolic acid may be entirely removed, while the larger part of the hydroxy acid remains behind, dissolved in the hot water. The solution was filtered from a small amount of tarry matter and, when cold, was extracted with ether.

[1] This JOURNAL, 17, 432. [2] *Ibid*, 17, 433.
[3] J. Chem. Soc. 67, 341, (1895).

On evaporating the ether and drying *in vacuo* over sulphuric acid the hydroxylauronic acid remains as a viscous, hygroscopic liquid. For analysis the acid was dried for a short time at 105°.

0.1248 gram of the acid gave 0.1068 gram H_2O and 0.2855 gram CO_2.

0.1098 gram of the acid gave 0.0898 gram H_2O and 0.2524 gram CO_2.

	Calculated for $C_8H_{14}<^{CO_2H}_{OH}$	Found. I.	II.
C	62.79	62.39	62.69
H	9.30	9.51	9.09

The *copper salt*, $\left(C_8H_{14}<^{CO_2}_{OH}\right)_2Cu + H_2O$, was prepared, by precipitation, from the easily soluble calcium salt. When air-dry the salt contains 1 molecule of water of crystallization, but this is partly lost on standing over sulphuric acid. The salt is green and very difficultly soluble in water.

0.1224 gram of the salt lost 0.0051 gram H_2O at 105°.

0.0796 gram of the salt lost 0.00315 gram H_2O at 105°.

	Calculated for $(C_8H_{14}<^{CO_2}_{OH})_2Cu + H_2O$.	Found. I.	II.
H_2O	4.25	4.16	3.96

0.1173 gram of the dry salt gave 0.0235 gram CuO.

0.1000 gram of the dry salt gave 0.0197 gram CuO.

	Calculated for $(C_8H_{14}<^{CO_2}_{OH})_2Cu$.	Found. I.	II.
Cu	15.88	16.00	15.73

If the views which have been expressed are correct, the hydroxyl group of hydroxylauronic acid is that of a secondary alcohol and is in the β position with reference to the carboxyl. A very strong confirmation of this opinion is given by the conduct of the acid toward Beckmann's chromic acid mixture.[1] While this mixture is without effect on dihydrohydroxycampholytic acid in the cold, it darkens quickly when added to hydroxylauronic acid and there is, at the same time, a slow evolution of carbon dioxide. Evidently the mixture converts the secondary hydroxyl into carbonyl and, as the resulting

[1] Ann. Chem. (Liebig), **250**, 325.

acid is a β-ketonic acid, it undergoes decomposition, in accordance with the well-known law for such acids, yielding carbon dioxide and a ketone. As the hydroxy acid is difficult to obtain, the ketone has not yet been isolated in pure condition.

Dihydro-cis-campholytic Acid.

This acid is readily obtained by reducing cis-campholytic acid with amyl alcohol and sodium. After purification by treatment of the solution of the sodium salt with an excess of potassium permanganate, the acid is an oily liquid, almost insoluble in water, and having an odor somewhat like that of valerianic acid. It boils at 244°. The boiling-point of cis-campholytic acid, which has not yet been given, was also determined and found to be at 255°–256°. The boiling-point of the cis-trans-campholytic acid is 240°–243°, very near to that of the dihydrociscampholytic acid. The specific gravity of the dihydro acid at 20° is 0.9833.[1] The acid is perfectly stable toward a cold solution of potassium permanganate. The composition of the acid was established by analyses, but the record was unfortunately lost in a fire.

The *amide*,[1] $C_8H_{18}CONH_2$, was prepared by treating the acid with phosphorus pentachloride and pouring the product carefully into cooled aqueous ammonia. It crystallizes from alcohol of 30 per cent. in needles, while from strong alcohol it separates in good-sized, rectangular plates. It is remarkably stable toward potassium permanganate, and may even be crystallized unchanged from a boiling, dilute solution of the salt. It melts at 161°.

α-Bromdihydro-cis-campholytic Acid.

This was prepared by treating the acid with phosphorus pentachloride and with bromine, as directed by Baeyer[2] and Aschan.[3] After decomposing the chloride of the acid by warming with formic acid the acid was crystallized from formic acid and the crystals washed with ligroïn. The acid melts at 129°–130°. It crystallizes from formic acid in needles.

[1] Preparation and determination by Mr. E. B. Harris.
[2] Ann. Chem. (Liebig), **245**, 175. [3] *Ibid.*, **271**, 265.

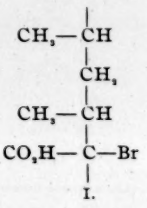
The record of the bromine determinations, which established the composition, was lost.

When α-bromdihydro-cis-campholytic acid is treated with a cold alcoholic solution of potash, hydrobromic acid is removed and cis-campholytic acid is regenerated. The acid was identified by its melting-point, crystalline form and by the melting-point of its amide. This furnishes a new and positive proof that the double union of cis-campholytic acid is in the α-β-position, and gives additional support to the view expressed in my last paper that the two campholytic acids are stereoisomers.

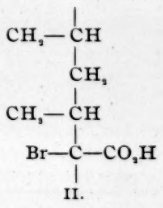
Attempts to reduce cis-trans-campholytic acid by amyl alcohol and sodium or by any other methods have, thus far, been entirely unsuccessful.

Hexahydroxylylic Acid.

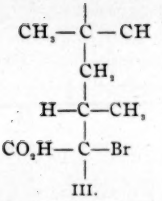
The proof that cis-campholytic acid is regenerated from the α-bromdihydrocampholytic acid, together with the fact that cis-campholytic acid is optically inactive has made it possible to subject Armstrong's formula to a synthetic test, which is nearly or quite conclusive. According to Armstrong's formula cis-campholytic acid must be Δ^1-tetrahydroxylylic acid. The reduction of xylylic acid $\left(C_6H_3\begin{cases}CH_3 & (1)\\ CH_3 & (3)\\ CO_2H & (4)\end{cases}\right)$, would give, apart from enantiomorphic forms, four stereoisomers, corresponding to which there would be four α-bromhexahydroxylylic acids. These would have the configuration represented by the following formulæ, in which only the atoms concerned in the stereoisomerism are shown :



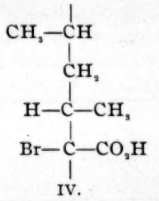
I.



II.



III.



IV.

Of these isomers, I and IV, supposing Armstrong's formula to be correct, would give cis-campholytic acid directly when treated with alcoholic potash. II and III would give either cis-trans-campholytic acid or a Δ^{8}-tetrahydroxylylic acid.

Xylylic acid (melting-point 126°) was reduced with amyl alcohol and sodium, the reduction being several times repeated to secure as complete a conversion as possible. The hexahydroxylylic acid was purified by treatment with potassium permanganate and distillation with water vapor. The acid came over as an oil which soon solidified, the first portions melting a little below and the later portions a little above 60°. The composition of the acid was established by analyses, but the record was burned, and as the point for which the experiments were undertaken has been established, it has not been deemed necessary to repeat the work. From the hexahydro acid the α-brom derivative was prepared, and this also was analyzed. The record of its melting-point was lost and is of little consequence, as it was probably a mixture of stereoisomers. On treatment with alcoholic potash, the main product of the action was a liquid acid which was not cis-trans-campholytic acid, since it was not converted into cis-campholytic acid by the action of dilute sulphurie acid (1 : 1). A very small amount of a solid acid melting at about 100° was found. While it is possible that the product consisted in part of the Δ^{6} tetrahydroxylylic acid, it seems scarcely possible that the Δ^{1} acid was not also formed. The properties of cis-campholytic acid are so characteristic that the body is easily identified, and it could scarcely have been overlooked, if present. The evidence appears to be conclusive, therefore,

that cis-campholytic acid is not Δ^1-tetrahydroxylylic acid and that Armstrong's formula for camphor is not true.

The results described in the latter part of this paper are of such a nature as to render a similar examination of the truth or falsity of Collie's formula for camphoric acid of very great interest. Mr. W. E. Burk has, under my direction, spent a considerable amount of time in attempting the preparation of the neighboring xylylic acid necessary for the purpose. The work has been thus far only partially successful, but will be continued.

DERIVATIVES OF DIHYDRO-CIS-CAMPHOLYTIC ACID.

By E. B. Harris.

The amide of dihydro-cis-campholytic acid has been described above. When treated with an alkaline solution of potassium hypobromite an amine, $C_8H_{18}NH_2$, is formed. The conversion was effected as follows: 8 grams of the amide were placed in a distilling-bulb and a freshly prepared solution of 8.2 grams of bromine in 100 cc. of ten per cent. sodium hydroxide was added. On warming gently the reaction took place, accompanied by some evolution of heat. The amine formed was distilled with water vapor and collected in dilute hydrochloric acid.

The *chloride*, $C_8H_{18}NH_2.HCl$, crystallizes in needles which are easily soluble in water and alcohol and melt with decomposition at 239°.

The *sulphate* crystallizes in white scales which are rather difficultly soluble in water. It resembles somewhat the sulphate of the ethyl ester of aminolauronic acid.

The *chloroplatinate*, $(C_8H_{18}NH_2)_2H_2PtCl_6$, crystallizes from hot water, in which it is difficultly soluble, in fine, light-orange colored needles.

0.0998 gram of the salt gave 0.0287 gram Pt.
0.1120 " " " " 0.0325 " "
0.1587 " " " " 0.0465 " "

	Calculated for $(C_8H_{18}NH_2)_2H_2PtCl_6$.	Found. I.	II.	III.
Pt	29.36	28.75	29.01	29.30

The free amine, $C_8H_{15}NH_2$, is a clear, colorless, mobile liquid with a very characteristic ammoniacal, fishy odor. It is slightly soluble in water, easily in alcohol and ether. It boils at 156°.5. Its specific gravity at 20° is 0.8431.

Alcohol, $C_8H_{15}OH$.

In order to obtain, if possible, the alcohol corresponding to the amine, three grams of the latter were converted into the sulphate by means of dilute sulphuric acid, the solution was rendered slightly alkaline with caustic soda and the theoretical amount of a strong solution of sodium nitrite was added. Decomposition took place slowly with a slight evolution of heat. A greenish yellow oil, having a marked odor of turpentine, separated on top. The products of decomposition were roughly separated by distilling twice with water vapor. The portion which came over first, after separating from the water and drying, consisted of a light, somewhat volatile oil which boiled at about 122°. It was undoubtedly a hydrocarbon, C_8H_{14}. It is evident that the decomposition, as is so often the case with cyclic amines, takes place mainly with the formation of this hydrocarbon instead of the alcohol desired. During the distillation there separated in the condenser a small amount of a white, crystalline, rather volatile substance, which melts at 59°. It was soluble in ether, insoluble in water, and stable toward permanganate. A test with phenylhydrazine indicated that it was not a ketone. The body was not obtained in sufficient amount for analysis.

The portion of the distillate referred to above, which was supposed to contain the alcohol, $C_8H_{15}OH$, was extracted with ether, and after evaporation of the ether the residue was heated to 55°–60° for twenty minutes with 3 cc. of Beckmann's mixture[1] of sulphuric acid and potassium pyrochromate. The ketone formed was extracted with ether, washed with water and sodium hydroxide and, after the removal of the ether, distilled with water vapor. It was then converted into the oxime by treatment with hydroxylamine chloride and sodium carbonate in dilute alcoholic solution. The oxime obtained crystallizes in needles or small prisms, has an odor resembling

[1] Ann. Chem. (Liebig), **250**, 325.

that of camphor oxime and melts at 112°–113°. The amount obtained was too small for satisfactory purification, but crystallization from a very small amount of alcohol did not change the melting-point.

This oxime proves to be of very unusual interest, because of its very close agreement in properties with the oxime of Kipping's dimethyl-(1.3)-cyclohexenone-(2). Kipping's[1] oxime melts at 114°–115°, and in its other properties agrees with this oxime as far as can be determined. Not much reliance can be placed on the melting-point as a proof of identity in this case, however, since Zilinsky[2] has recently obtained the same oxime, having prepared the ketone by a somewhat different method and gives a melting-point of 104°–105°. We have also prepared the oxime as follows: Pentanetetracarboxylic ester was prepared from trimethylene bromide and malonic ester according to Baeyer's directions;[3] the two methyl groups were introduced as directed by Perkin and Prentice;[4] the resulting ester was saponified with methyl alcoholic potash; the tetracarboxylic acid was decomposed by heating to about 200°, and the resulting dimethylpimelic acid was distilled under diminished pressure. The acid was mixed with twice its weight of lime and, after fractioning, the ketone obtained was converted into the oxime. The oxime obtained melted at 120°–122°.

A comparison of these results seems to indicate that the ketone, or at least, the oxime, was, in each case, a mixture of stereomeric modifications. While the evidence that the oxime derived from cis-campholytic acid is in reality a derivative of the dimethyl-(1.3)-hexanone-(2) is unsatisfactory, there is some probability that it has this structure. The synthesis of the Δ^1-tetrahydro-(1. 2. 3)-xylylic acid, which, if this is true, must have the same structure as campholytic acid, will furnish positive evidence on this point. Experiments for this purpose have already been commenced.

TERRE HAUTE, INDIANA, JULY 31, 1896.

[1] J. Chem. Soc., **67**, 351, (1895).
[2] Ber. d. Chem. Ges., **28**, 781.
[3] Ann. Chem. (Liebig), **278**, 100.
[4] Ber. d. chem. Ges., **24**, 818, 852.

Contribution from the Sheffield Laboratory of Yale University.

ON DIACID ANILIDES.

By H. L. Wheeler.

For convenience of reference, diacid anilides may be divided into two classes. The first class will consist of those which have identical acid groups, such as diacetanilide,

$$C_6H_5.N<\begin{matrix}COCH_3\\COCH_3\end{matrix},$$

while the second class will contain those with unlike acid groups, and will be referred to as mixed diacid anilides, formylacetanilide, for example,

$$C_6H_5.N<\begin{matrix}CHO\\COCH_3\end{matrix}.$$

Diacid anilides of the first class can be prepared by acting on the mono acid anilides with acid anhydrides[1][2] or acid chlorides.[3] They have also been obtained from the sodium salts of the anilides and acid anhydrides[4] and from the mustard oils.[5]

Diacid anilides of the second class have not been obtained by any of the above methods. They could not be prepared by acting on the monoacid anilides[6] or their sodium salts[7] with acid chlorides, while attempts to prepare them by acting on the anilides with acid anhydrides, formanilide, and acetic anhydride, for example, did not give pure products. However, the above method can be used with success in the preparation of what may be called semi-diacid anilides, since oxanilide and oxalparatoluide give monoacetyloxanilide and monoacetyloxalparatoluide,[8] *i. e.*,

$$\begin{matrix}CO.N<\begin{matrix}COCH_3\\C_6H_5\end{matrix}\\|\\CO.NHC_6H_5\end{matrix} \quad \text{and} \quad \begin{matrix}CO.N<\begin{matrix}COCH_3\\C_6H_4CH_3\end{matrix}\\|\\CO.NHC_6H_4CH_3\end{matrix}$$

In two former papers[9] from this laboratory the action of benzoyl chloride on the silver and mercury salts of the ani-

[1] Bistrzycki and Ulffers: Ber. d. chem. Ges., **27**, 91.
[2] Tassinari: *Ibid*, R, **27**, 581.
[3] Kay: *Ibid*, **26**, 2853.
[4] Blacher: *Ibid*, **28**, 2356.
[5] Kay: *Ibid*, **26**, 2848.
[6] Pictet: *Ibid*, **23**, 3014.
[7] Paal and Otten: *Ibid*, **23**, 2587.
[8] Tassinari: *Loc. cit.*
[9] Wheeler and Boltwood: This Journal, **18**, 381; Wheeler and McFarland, *Ibid*, **18**, 540.

lides was described. It was then shown that these salts could be used for the synthesis of the hitherto inaccessible mixed diacid anilides, and that both silver and mercury formanilide gave the same compound, *i. e.*, formylbenzanilide $C_6H_5N<^{CHO}_{COC_6H_5}$, etc.

In the present paper it will be shown that the action of aliphatic acid chlorides on silver formanilide and mercury acetanilide is perfectly analogous to that of benzoyl chloride; that the formation of mixed diacid anilides is general; and that these diacid anilides react with alkali invariably with the separation of the lower acid radical and formation of the anilide of the higher acid, as follows:

$$C_6H_5N<^{CHO}_{COCH_3} + NaOH = C_6H_5N<^{H}_{COCH_3} + NaOCHO.$$

By this reaction the mixed diacid anilides are shown to be nitrogen derivatives, and, since diacetanilide is formed from the mercury salt of acetanilide in precisely the same manner as the mixed diacid anilides, it is probable that the anilides of both classes have an analogous structure.

In the latter part of this paper a notice is given of the action of acetyl and benzoyl chlorides on silver and mercury benzamide, and it is the intention of the author to extend the work to salts of other amides and imides.

From silver formanilide and mercury acetanilide the following series of diacid anilides have now been prepared in this laboratory:

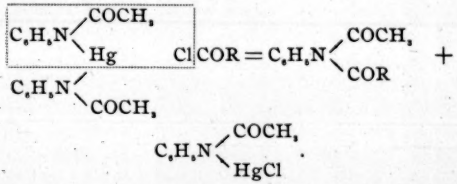
Acetylacetanilide or Diacetanilide,

Formylacetanilide,	Acetylpropionanilide,
Formylpropionanilide,	Acetyl-*n*-butyranilide,
Formyl-*n*-butyranilide,	Acetylisovaleranilide,
Formylstearanilide,	Acetylpalmitanilide,
Formylbenzanilide,	Acetylbenzanilide.

Method of Preparation.

Silver formanilide or mercury acetanilide was suspended in dry ether or benzene and 1 molecular proportion of acid chloride was added. In the case of the mercury salts it was found convenient to use only 1 molecular proportion of acid

chloride, since, by this means, the presence of mercuric chloride in the extract was largely avoided. The action then takes place chiefly as follows:



The action begins immediately with evolution of heat and is complete in the case of the lower acid chlorides in a few minutes. After filtering from the silver chloride or the halogen mercuric compound, the filtrates in the case of the lower acid derivatives, were shaken with water, and on evaporating the solvent the diacid anilides were obtained as oils. The purification and properties of these products are described below.

Acetylacetanilide or Diacetanilide, $C_6H_5N{<}^{COCH_3}_{COCH_3}$.—The preparation of this compound has received considerable attention. Bistrzycki and Ulffers[1] have carefully investigated the formation from acetanilide and acetic anhydride and conclude that it is not to be obtained in a pure condition by the method of Reverdin and de la Harpe.[2] They have shown that it can not be obtained from aniline and acetic acid as stated by Gumpert[3], and they also call attention to the fact that Krafft and Karsten[4] have shown that Hofmann[5] did not obtain this compound from phenyl mustard oil and acetic acid. They state that they obtained diacetanilide first in April, 1893. They were anticipated, however, by Kay,[6] who prepared this compound from phenyl mustard oil and acetic anhydride, as well as from acetanilide and acetyl chloride. Its preparation, according to the method of Bistrzycki and Ulffers has been confirmed by Tassinari,[7] while Blacher[8] obtained it from

[1] *Loc cit.*
[2] Ber. d. chem. Ges., **22**, 1006.
[3] J. prakt. Chem. [2], **32**, 294.
[4] Ber. d. chem. Ges., **25**, 460.
[5] *Ibid*, **3**, 770.
[6] *Loc. cit.*
[7] *Loc. cit.*
[8] *Loc. cit.*

sodium acetanilide and acetic anhydride. The work of the later investigators confirms that of Kay, and they refer to him for the properties of this compound. He obtained this diacid anilide as a clear colorless oil, boiling at 150° at 16 mm. pressure and solidifying to a mass of crystals, which on crystallizing from ligroïn melted at 37°.

The same compound results by acting on mercury acetanilide with acetyl chloride. The product obtained from the benzene solution, in this case, was an oil which boiled at 150° at 17 mm. pressure and the distillate soon solidified to a colorless mass of crystals, which on crystallizing from ligroïn separated in eight-sided plates, melting at 37°. On warming with a dilute alcoholic solution of sodium hydroxide, acetanilide was formed.

Formylacetanilide, $C_6H_5N<^{CHO}_{COCH_3}$.—This was obtained as an oil which soon solidified. It was crystallized from a mixture of ether and ligroïn, by evaporation under diminished pressure, when beautiful, colorless, prismatic crystals were obtained, melting at 56°.

	Found.	Calculated for $C_9H_9NO_2$.
N	8.59	8.58

Formylacetanilide is readily soluble in alcohol, ether, and benzene, but difficultly in ligroïn. On boiling with dilute sodium hydroxide it dissolves, and, on cooling, acetanilide separates in plates melting at 114°.

Formylpropionanilide, $C_6H_5N<^{CHO}_{COCH_2CH_3}$.—The product of the action of propionyl chloride on both silver and mercury formanilides, in ether or benzene, either when obtained directly or when first shaken with bicarbonate of soda, was an oil which did not solidify in a freezing-mixture. On attempting to purify it by distillation, at 18 mm. pressure, it decomposed with effervescence, the pressure increased, and, finally, when this ceased, propionanilide distilled over, boiling at 183° at 20 mm. pressure. The decomposition possibly took place as follows:

$$C_6H_5N<^{CHO}_{COCH_2CH_3} = C_6H_5N<^{H}_{COCH_2CH_3} + CO.$$

The oil gave propionanilide[1] melting at 105° when boiled with dilute sodium hydroxide.

Formylnormalbutyranilide, $C_6H_5N<\begin{matrix}CHO\\CO(CH_2)_3CH_3\end{matrix}$.—This diacid anilide was obtained only in the form of an oil and, like the preceding, it could not be solidified or distilled without decomposition. When an attempt was made to distil this crude product at 20 mm. pressure, it boiled from 164° to 185°. This fraction was distilled again at 20 mm. pressure, when the larger portion, a clear colorless oil, was collected between 172° and 180°. On standing, this fraction deposited plates, melting from 90 to 92°. The distillate was therefore a mixture of the diacid anilide with butyranilide.[2] The latter was obtained when the oil was boiled with dilute alcoholic sodium hydroxide.

Formylstearanilide, $C_6H_5N<\begin{matrix}CHO\\CO(CH_2)_{16}CH_3\end{matrix}$.—The stearic acid used in this experiment melted from 69° to 70°. From this the chloride was prepared according to the method of Krafft and Bürger.[3] In this case silver formanilide, suspended in ether, was used. On evaporating the ethereal solution minute, flattened, colorless crystals were obtained. These, on crystallizing repeatedly from ether, melted at 61°.

	Found.	Calculated for $C_{38}H_{41}NO_2$.
N	3.34	3.61

Formylstearanilide is extremely soluble in benzene, chloroform, ligroïn, and carbon disulphide, easily in ether, but less readily in cold alcohol. On heating the diacid anilide a decomposition takes place, as follows:

$$C_6H_5N<\begin{matrix}CHO\\CO(CH_2)_{16}CH_3\end{matrix} = C_6H_5NC + HOCO(CH_2)_{16}CH_3.$$

When the alcoholic solution is warmed with potassium hydroxide a bulky mass of colorless needles separates; these melt from 93° to 94°, and the product is therefore stearanilide.[4]

[1] Kelbe: Ber. d. chem. Ges., **16**, 1200.
[2] Gerhardt: Ann. Chem. (Liebig), **87**, 166.
[3] Ber. d. chem. Ges., **17**, 1380.
[4] Pebal: Ann. Chem. (Liebig), **91**, 152.

Acetylpropionanilide, $C_6H_5N<^{COCH_3}_{COCH_2CH_3}$.—The product in this case was distilled at 18 mm. pressure when a clear colorless oil was obtained, boiling from 159° to 160°, which did not solidify in a freezing-mixture.

	Found.	Calculated for $C_{11}H_{13}NO_2$.
N	7.46	7.33

Acetylpropionanilide is readily soluble in ether and benzene. When the analyzed substance was warmed with dilute sodium hydroxide and the product crystallized from dilute alcohol, plates of propionanilide were obtained, melting at 105°.

Acetylnormalbutyranilide, $C_6H_5N<^{COCH_3}_{CO(CH_2)_2CH_3}$, was obtained as a clear, colorless oil, boiling at 163° under 18 mm. pressure.

	Found.	Calculated for $C_{12}H_{15}NO_2$.
N	7.18	6.83

When warmed with sodium hydroxide in alcohol it gave butyranilide melting from 90° to 92°.

Acetylisovaleranilide, $C_6H_5N<^{COCH_3}_{COCH_2CH<^{CH_3}_{CH_3}}$.—The isovaleryl chloride used in this experiment boiled from 113 to 116°. The diacid anilide was an oil which was distilled at 18 mm. pressure. The fraction boiling at 161.5° to 167° was collected and redistilled at the same pressure, the larger portion then boiled between 164° and 165°.

	Found.	Calculated for $C_{13}H_{17}NO_2$.
N	6.46	6.39

The product obtained on boiling this with alcoholic sodium hydroxide was crystallized from dilute alcohol and finally from a mixture of ligroïn and benzene. It then melted at 115° and and was therefore isovaleranilide.[1]

Acetylpalmitanilide, $C_6H_5N<^{COCH_3}_{CO(CH_2)_{14}CH_3}$.—The palmitic acid used in this case melted from 61° to 62°. It was converted into the chloride according to the directions of

[1] Chiozza: Ann. Chem. (Liebig), **84**, 109.

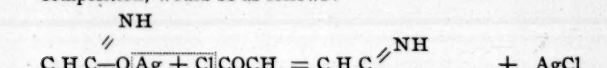
Krafft and Bürger.[1] The diacid anilide was obtained as an oil, which readily solidified. It was dissolved in cold ligroïn, filtered from a small amount of acetanilide (?), and the solution was then evaporated to dryness, the residue dissolved in alcohol, and the diacid anilide precipitated with a small amount of water. It was then crystallized several times from ether, a rather unsatisfactory operation on account of its great solubility. It was thus obtained as a compact mass of colorless, indistinct, microscopic crystals, melting from 60° to 61°.

	Found.	Calculated for $C_{14}H_{19}NO_3$.
N	3·54	3·75

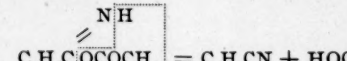
On warming this product with alcoholic potassium hydroxide it gave palmitanilide[2] melting from 90° to 91°.

Experiments with Silver and Mercury Benzamide.

It would be expected that the silver and mercury salts of the amides would react with acid chlorides in an analogous manner to the corresponding salts of the anilides, and that diacid amides would result as the chief products. This, however, is not the case with either silver or mercury benzamide. Although silver benzamide reacts with alkyl[3] halides precisely like silver formanilide,[4] *i. e.*, in both cases imidoethers result, on the other hand, with acid chlorides, silver and mercury benzamide give chiefly benzonitrile. This reaction, in the case of the silver salts, if represented as a direct double decomposition, would be as follows:



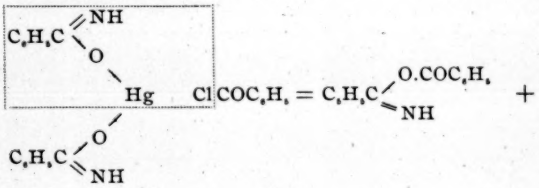
and

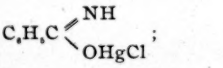


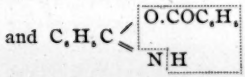
This apparently parallel reaction with alkyl halides would not be surprising if it were not for the entirely opposite reactions of the salts of the anilides.

[1] *Loc. cit.* [2] Hell and Jordanow: Ber. d. chem. Ges., **24**, 943.
[3] Tafel and Enoch: Ber. d. chem. Ges., **23**, 104.
[4] Comstock and Kleeburg: *Ibid*, **12**, 493.

In the case of the action of benzoyl chloride on mercury benzamide, using molecular proportions of the acid chloride, the yield of benzonitrile was about 72 per cent. of the calculated. A direct double decomposition in this case again would be represented as follows:





and 

While hitherto there has been no reason to assign to the salts of the amides a structure different from those of the anilides, this must now be done if the action of acid chlorides on these salts is a direct double decomposition, as shown above. For this reason these methods of representing the reactions are objectionable. It is far more probable that it is not the structure of the salts which varies in these tautomeric reactions, but that it is the mechanism of the reactions which undergoes change in different cases. It is probable in some cases that unstable addition-products[1] occur which break up into simpler products, and in other cases that double decompositions take place. The chief course of the reaction being influenced, not only by the union of the atoms or groups in the molecules reacting, but also by their chemical and physical nature and spacial arrangement.

NEW HAVEN, June, 1896.

[1] Nef: Ann. Chem. (Liebig), **287**, 269; and Proc. Amer. Acad., May, 1892, 169.

ol. 18
896

Contribution from the Chemical Laboratory of the Massachusetts Institute of Technology.

XIV.—IODOMETRIC DETERMINATION OF SELENIOUS AND SELENIC ACIDS.

By James F. Norris and Henry Fay.

The methods already in use for the volumetric determination of selenious acids are those of Muthmann and Schaefer,[1] and Gooch and Peirce.[2] The former method has been studied by Gooch and Reynolds,[3] and found to be inaccurate. The method of Gooch and Peirce depends upon the reduction of a known weight of potassium iodide in sulphuric acid solution by selenious acid in presence of arsenic acid. The difference between the arsenious acid equivalent to the potassium iodide and the amount found is a measure of the selenious acid. Selenic acid is first reduced by boiling with potassium bromide and sulphuric acid under definite conditions.

The method here proposed requires fewer reagents, occupies less time, and gives more accurate results. The determination depends on the reaction between sodium thiosulphate and selenious acid in presence of hydrochloric acid. So far we are unable to state the complete reaction which takes place, but have found that one molecule of selenious acid is exactly equivalent to four molecules of sodium thiosulphate. After standing about twenty-four hours, part of the selenium is precipitated. In neutral solution the reaction takes place slowly and is not complete after standing a day. In a strong neutral solution there is immediate precipitation of selenium, and the reaction becomes strongly alkaline. In this solution no sulphates were found. It is proposed to make a more complete study of this reaction.

The reagents used were carefully purified. Resublimed iodine was sublimed from one-third of its weight of potassium iodide and dissolved in potassium iodide free from iodate. This precaution was necessary as the titrations were made in acid solution. A hot concentrated solution of potassium iodide was boiled five minutes with the addition of a small quantity of hydrochloric acid, the solution cooled rapidly and

[1] Ber. d. chem. Ges., **26**, 1008. [2] Am. J. Sci., **1**, [4], 31.
[3] *Ibid*, **50**, 254.

the precipitate washed with alcohol to remove free iodine. The potassium iodide gave no reaction with starch when acidified with hydrochloric acid.

As the commercial sodium thiosulphate gave a different iodine-value in acid and neutral solution, it was found necessary to recrystallize it to remove the sulphite, although the presence of the latter was not indicated by barium chloride. The sodium thiosulphate was standardized against resublimed iodine and pure sodium arsenite.

The selenious acid was prepared from commercial selenium by evaporating to dryness with concentrated nitric acid. The selenium dioxide thus obtained was reduced by sodium sulphite and hydrochloric acid, and the pure selenium was again oxidized by evaporating to dryness with nitric acid, and the residue resublimed. In order to prevent reduction the oxide was sublimed in a small beaker, covered with a watch-glass, and containing a drop of strong nitric acid. By this method long, perfectly white needles of selenium dioxide can be obtained which are free from selenic acid. About 2 grams were weighed accurately, dissolved in water and diluted to 500 cc.

The selenic acid was prepared by dissolving about 2 grams of selenium dioxide in 200 cc. of water and adding a strong solution of potassium permanganate until a permanent pink color remained after heating one-half hour at 60° C. Sulphurous acid was then added until only a small amount of manganese dioxide remained, and the solution filtered and diluted to 500 cc. Sodium thiosulphate titrated in the presence of a definite portion of this solution acidified with hydrochloric acid, gave the same iodine-value as without its presence, thus showing the absence of selenious acid.

The flasks and burettes were calibrated according to the method of Morse and Blalock.[1]

Determination of Selenious Acid.

A definite portion of selenious acid was measured off, diluted with ice-water and 10 cc. hydrochloric acid (1.12 sp. gr.) An excess of one-tenth normal solution of sodium thiosulphate was added and titrated back with iodine solution.

[1] This JOURNAL, 16, 479.

One molecule selenious acid, SeO_2, is equivalent to four molecules of thiosulphate, $Na_2S_2O_3.5H_2O$. It was found necessary to have enough hydrochloric acid present to set free all of the thiosulphuric acid. If the solution is cold a large excess of hydrochloric acid does not affect the titration. The following is a series of eight consecutive determinations :

SeO_2 taken.	SeO_2 found.	SeO_2 taken.	SeO_2 found.
0.0829	0.0829	0.1366	0.1367
0.0829	0.0829	0.1366	0.1368
0.1242	0.1242	0.1656	0.1659
0.1242	0.1242	0.2070	0.2071

It will be seen that the error varies from 0.00 to 0.18 per cent., the average being 0.06 per cent. The method is therefore one of the most accurate of iodometric methods and can be used conveniently for the standardization of sodium thiosulphate. The solution of selenious acid is entirely stable.

Determination of Selenic Acid.

As selenic acid does not react with sodium thiosulphate, it is first reduced by boiling with hydrochloric acid and titrated as above. It was found necessary to modify the method of Gooch and Evans' for the reduction by hydrochloric acid, as there was invariably loss of selenium.

To a measured portion of selenic acid is added 25 cc. concentrated hydrochloric acid and the solution diluted to 100 cc. The solution is boiled for one hour, precaution being taken not to allow the volume to go below 75 cc., cooled, diluted with ice-water and the selenious acid determined by titration. The following results were obtained consecutively :

SeO_3 taken.	SeO_2 found.	SeO_3 taken.	SeO_2 found.
0.1011	0.1009	0.1598	0.1595
0.1011	0.1008	0.1598	0.1595
0.1067	0.1067	0.2023	0.2024
0.1067	0.1065	0.2665	0.2662

Determination of a Mixture of Selenious and Selenic Acids.

Two portions of a solution containing a known quantity of selenious and selenic acids were measured off. In one the selenious acid was determined by direct titration; in the other the total selenium, after reduction of the selenic acid, was determined. On heating the solution in the reduction of selenic acid, some selenium is precipitated, which goes into solution

[1] Am. J. Sci., 50, 400.

when the chlorine is evolved. The method was tested by the following determinations:

SeO_2 taken.	SeO_2 found.	SeO_2 taken.	SeO_2 found.
0.0467	0.0467	0.1013	0.1015
0.0467	0.0466	0.1013	0.1016
0.0934	0.0933	0.0506	0.0504
0.1868	0.1865	0.1012	0.1015

BOSTON, MASS.

NOTE.

To the Editor: In the July number of the JOURNAL there is a preliminary notice on the "Aluminum Alcoholates" by Mr. H. W. Hillyer, dated May 29. I beg to state that on May 2 I read before the Russian Chemical Society a paper "On the Action of Amalgamated Aluminum on Absolute Alcohols," of which the following abstract appeared in the "Proceedings of the Section of Chemistry of the Russian Physico-Chemical Society" ("Journal of the Russian Physico-Chemical Society," Vol. **28**, p. 412), and also in the "Chemiker Zeitung, Vol. **20**, No. 57, p. 563: "Amalgamated aluminum not only removes the last trace of moisture from alcohols, as has been observed by Wislicenus and Kaufmann (Ber. d. chem. Ges., **28**, 1323, 1983), but it also reacts with the alcohols forming aluminum alcoholates identical with the compounds described by Gladstone and Tribe (Trans. of the Chemical Society, 1881, p. 1). The following alcoholates have been prepared by heating the alcohols with amalgamated aluminum on the water-bath; their boiling-points have been determined for the first time:

	Melting point.	Boiling point 12 mm. press.	Al_2O_3 found.	Calculated for
Aluminum trimethylate	Decomposes when heated.		43.67%	$Al(CH_3O)_3$, 42.50%
" triethylate	132–136°	207–209°	32.13%	$Al(C_2H_5O)_3$, 31.47%
" tripropylate	99–105°	263–264°	26.31% 25.65% 25.63%	$Al(C_3H_7O)_3$, 25.00%
" triisobutylate	210–212°	250–254°	21.17%	$Al(C_4H_9O)_3$, 20.73%

The alcoholates burn in the air with a brilliant flame, and readily absorb water, the alcohols being regenerated. The investigation will be continued. It is proposed to investigate the action of amalgamated aluminum on secondary and tertiary alcohols, the reactions of aluminum alcoholates, and the action of other amalgamated metals on alcohols."

Yours truly,

W. TISTSCHENKO.

ST. PETERSBURG, IMP. UNIVERSITY,
CHEMICAL LABORATORY, Aug. 3, 1896.